EC-Lab®
Software
User's Manual

Version 10.1x – February 2011

Equipment installation

WARNING!: The instrument is safety ground to the Earth through the protective conductor of the AC power cable.

Use only the power cord supplied with the instrument and designed for the good current rating (10 Amax) and be sure to connect it to a power source provided with protective earth contact.

Any interruption of the protective earth (grounding) conductor outside the instrument could result in personal injury.

Please consult the installation manual for details on the installation of the instrument.

General description

The equipment described in this manual has been designed in accordance with EN61010 and EN61326 and has been supplied in a safe condition. The equipment is intended for electrical measurements only. It should be used for no other purpose.

Intended use of the equipment

This equipment is an electrical laboratory equipment intended for professional and intended to be used in laboratories, commercial and light-industrial environments. Instrumentation and accessories shall not be connected to humans.

Instructions for use

To avoid injury to an operator the safety precautions given below, and throughout the manual, must be strictly adhered to, whenever the equipment is operated. Only advanced user can use the instrument.
Bio-Logic SAS accepts no responsibility for accidents or damage resulting from any failure to comply with these precautions.

GROUNDING

To minimize the hazard of electrical shock, it is essential that the equipment be connected to a protective ground through the AC supply cable. The continuity of the ground connection should be checked periodically.

ATMOSPHERE

You must never operate the equipment in corrosive atmosphere. Moreover if the equipment is exposed to a highly corrosive atmosphere, the components and the metallic parts can be corroded and can involve malfunction of the instrument.
The user must also be careful that the ventilation grids are not obstructed. An external cleaning can be made with a vacuum cleaner if necessary.
Please consult our specialists to discuss the best location in your lab for the instrument (avoid glove box, hood, chemical products, …).

AVOID UNSAFE EQUIPMENT

The equipment may be unsafe if any of the following statements apply:

- Equipment shows visible damage,
- Equipment has failed to perform an intended operation,
- Equipment has been stored in unfavourable conditions,
- Equipment has been subjected to physical stress.

In case of doubt as to the serviceability of the equipment, don't use it. Get it properly checked out by a qualified service technician.

LIVE CONDUCTORS

When the equipment is connected to its measurement inputs or supply, the opening of covers or removal of parts could expose live conductors. Only qualified personnel, who should refer to the relevant maintenance documentation, must do adjustments, maintenance or repair

EQUIPMENT MODIFICATION

To avoid introducing safety hazards, never install non-standard parts in the equipment, or make any unauthorised modification. To maintain safety, always return the equipment to Bio-Logic SAS for service and repair.

GUARANTEE

Guarantee and liability claims in the event of injury or material damage are excluded when they are the result of one of the following.

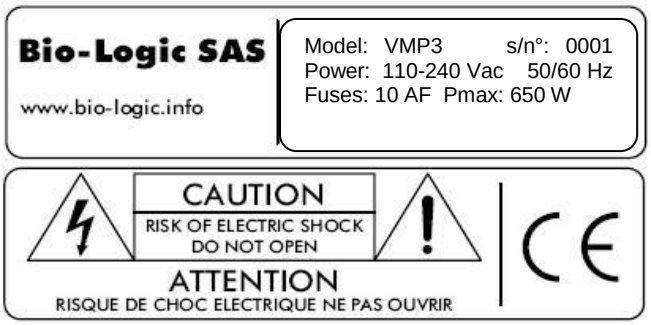
- Improper use of the device,
- Improper installation, operation or maintenance of the device,
- Operating the device when the safety and protective devices are defective and/or inoperable,
- Non-observance of the instructions in the manual with regard to transport, storage, installation,
- Unauthorized structural alterations to the device,
- Unauthorized modifications to the system settings,
- Inadequate monitoring of device components subject to wear,
- Improperly executed and unauthorized repairs,
- Unauthorized opening of the device or its components,
- Catastrophic events due to the effect of foreign bodies.

IN CASE OF PROBLEM

Information on your hardware and software configuration is necessary to analyze and finally solve the problem you encounter.

If you have any questions or if any problem occurs that is not mentioned in this document, please contact your local retailer (list available following the link: http://www.bio-logic.info/potentiostat/distributors.html). The highly qualified staff will be glad to help you.
Please keep information on the following at hand:

- Description of the error (the error message, mpr file, picture of setting or any other useful information) and of the context in which the error occurred. Try to remember all steps you had performed immediately before the error occurred. The more information on the actual situation you can provide, the easier it is to track the problem.
- The serial number of the device located on the rear panel device.



- The software and hardware version you are currently using. On the Help menu, click About. The displayed dialog box shows the version numbers.
- The operating system on the connected computer.
- The connection mode (Ethernet, LAN, USB) between computer and instrument.

General safety considerations

Class I

The instrument is safety ground to the Earth through the protective conductor of the AC power cable.

Use only the power cord supplied with the instrument and designed for the good current rating (10 A max) and be sure to connect it to a power source provided with protective earth contact.

Any interruption of the protective earth (grounding) conductor outside the instrument could result in personal injury.

Guarantee and liability claims in the event of injury or material damage are excluded when they are the result of one of the following.

- Improper use of the device,
- Improper installation, operation or maintenance of the device,
- Operating the device when the safety and protective devices are defective and/or inoperable,
- Non-observance of the instructions in the manual with regard to transport, storage, installation,
- Unauthorised structural alterations to the device,
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- Inadequate monitoring of device components subject to wear,
- Improperly executed and unauthorised repairs,
- Unauthorised opening of the device or its components,
- Catastrophic events due to the effect of foreign bodies.

ONLY QUALIFIED PERSONNEL should operate (or service) this equipment.

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1. Introduction

EC-Lab® software has been designed and built to control all of our potentiostats (single SP-150, SP-300, SP-200 or multichannel: MPG, VMP, VMP2(Z), BiStat, VMP3, VSP, and HCP-803). Each channel board of our multichannel instruments is an independent potentiostat/galvanostat that can be controlled by EC-Lab® software.

Each channel can be set, run, paused or stopped, independently of each other, using identical or different protocols. Any settings of any channel can be modified during a run, without interrupting the experiment. The channels can be interconnected and run synchronously, for example to perform multi-pitting experiments using a common counter-electrode in a single bath.

One computer (or eventually several for multichannel instruments) connected to the instrument can monitor the system. The computer can be connected to the instrument through an Ethernet connection or with an USB connection. With the Ethernet connection, each one of the users is able to monitor his own channel from his computer. More than multipotentiostats, our instruments are modular, versatile and flexible multi-user instruments.

Once the protocols have been loaded and started from the PC, the experiments are entirely controlled by the instrument's on-board firmware. Data are temporarily buffered in the instrument and regularly transferred to the PC, which is used for data storage, on-line visualization and off-line data analysis and display.
This architecture ensures very safe operations since a shutdown of the monitoring PC does not affect the experiments in progress.

The application software package provides useful protocols for general electrochemistry, corrosion, batteries, super-capacitors, fuel cells and custom applications. Usual electrochemical techniques, such as Cyclic Voltammetry, Chronopotentiometry, etc…, are obtained by associations of elementary sequences.

Conditional tests can be performed at various levels of any sequence on the working electrode potential or current, on the counter electrode potential, or on the external parameters. These conditional tests force the experiment to go to the next step or to loop to a previous sequence or end the sequence.

Standard graphic functions such as re-scaling, zoom, linear and log scales are available. The user can also overlay curves to make data analyses (peak and wave analysis, Tafel, R_p, linear fits, EIS simulation and modeling, …).

Post processing is possible using built-in options to create variables at the user's convenience, such as derivative or integral values, etc... Raw data and processed data can be exported as standard ASCII text files.

The aim of this manual is to guide the user in EC-Lab® software discovery. This manual is composed of several chapters. The first is an introduction. The second and third parts describe the software and give an explanation of the different techniques and protocols offered by EC-Lab®. Finally, some advanced features and troubleshooting are described in the two last parts.

It is assumed that the user is familiar with Microsoft Windows© and knows how to use the mouse and keyboard to access the drop-down menus.

WHEN AN USER RECEIVES A NEW UNIT FROM THE FACTORY, THE SOFTWARE AND FIRMWARE ARE INSTALLED AND UPGRADED. THE INSTRUMENT IS READY TO BE USED. IT DOES NOT NEED TO BE UPGRADED. WE ADVISE THE USERS TO READ AT LEAST THE SECOND AND THIRD CHAPTERS BEFORE STARTING AN EXPERIMENT.

2. EC-Lab® software: settings

2.1 Starting the Program

Double click on the EC-Lab® icon on the desktop. EC-Lab® software main window will be displayed:

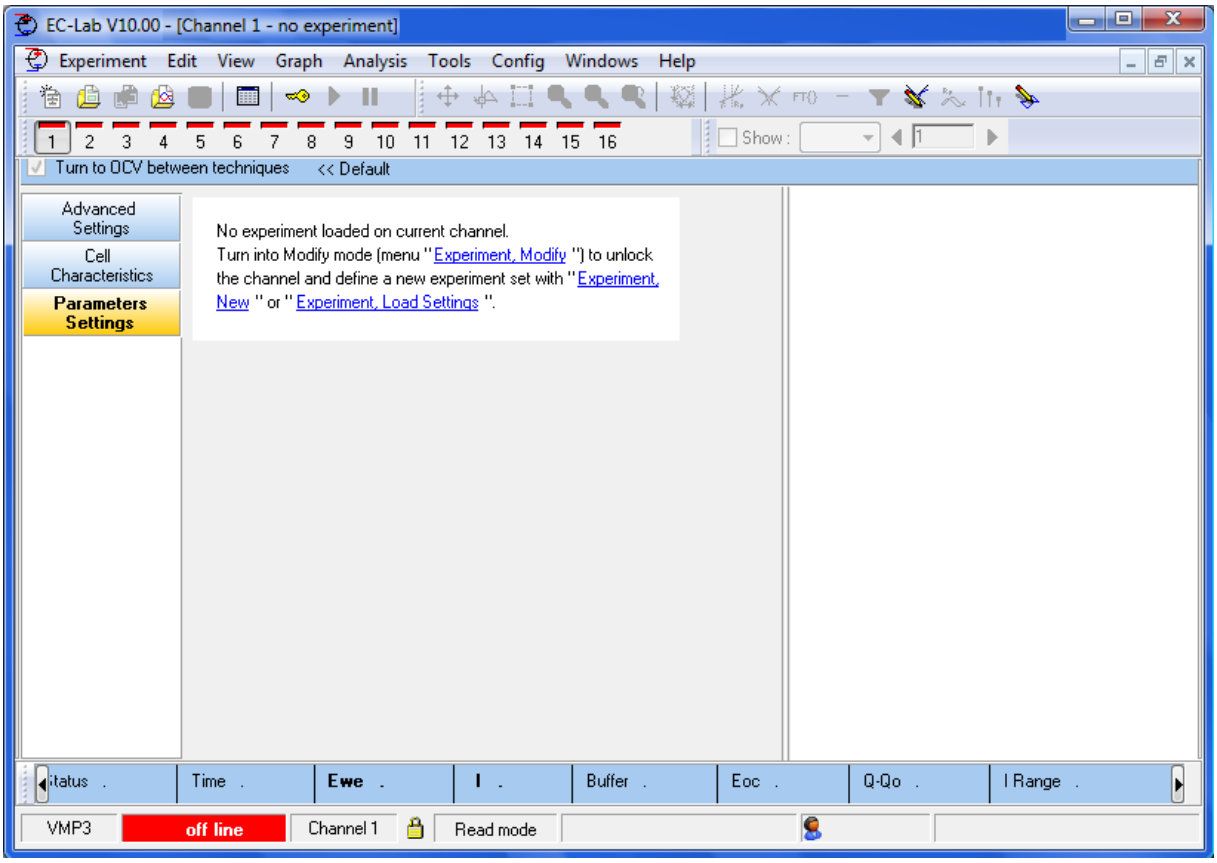

EC-Lab V10.00 - [Channel 1 - no experiment]
Experiment Edit View Graph Analysis Tools Config Windows Help
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Show :
Turn to OCV between techniques
<< Default
Advanced Settings
Cell Characteristics
Parameters Settings
No experiment loaded on current channel.
Turn into Modify mode (menu "Experiment, Modify ") to unlock the channel and define a new experiment set with "Experiment, New " or " Experiment, Load Settings ".
Time
Ewe
I
Buffer
Eoc
Q-Qo
I Range
VMP3
off line
Channel 1
Read mode

Fig. 1: Starting main EC-Lab® window.

Immediately on the main window, the following Username window will appear:

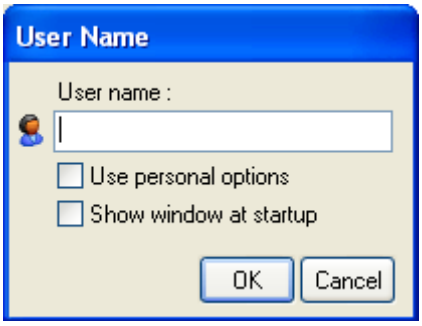


Fig. 2: User name window.

Type your username (*example : My Name*), and click **OK** or press < ENTER >.

This username is used as a safety password when the instrument is shared with several users. When you run an experiment on a channel, this code will be automatically transferred to the section "user" on the bottom of EC-Lab® software window. This allows the user to become the owner of the channel for the duration of the experiment. All users are authorized to view the channels owned by the other users. However, change of parameters on a channel is authorized only if the present username corresponds to the owner of that channel (even from another computer). If another user wants to modify parameters on a channel that belongs to "My Name", the following message appears:

"**Warning, channel X belongs to "My Name". By accepting modification you will replace current owner. Do you want to continue?"**

The command **User**... in the **Config.** menu allows you to change the username at any time. You can also double click on the “User “ section in the bottom of the EC-Lab® software window to change the username.

The user can specify a personal configuration (color display, tool bar buttons and position, default settings), which is linked to the username. If it is not selected, the default configuration is used.
For the user’s convenience it is also possible to hide this window when EC-Lab® software is starting.
When the username is set, the “Global View” window is displayed:

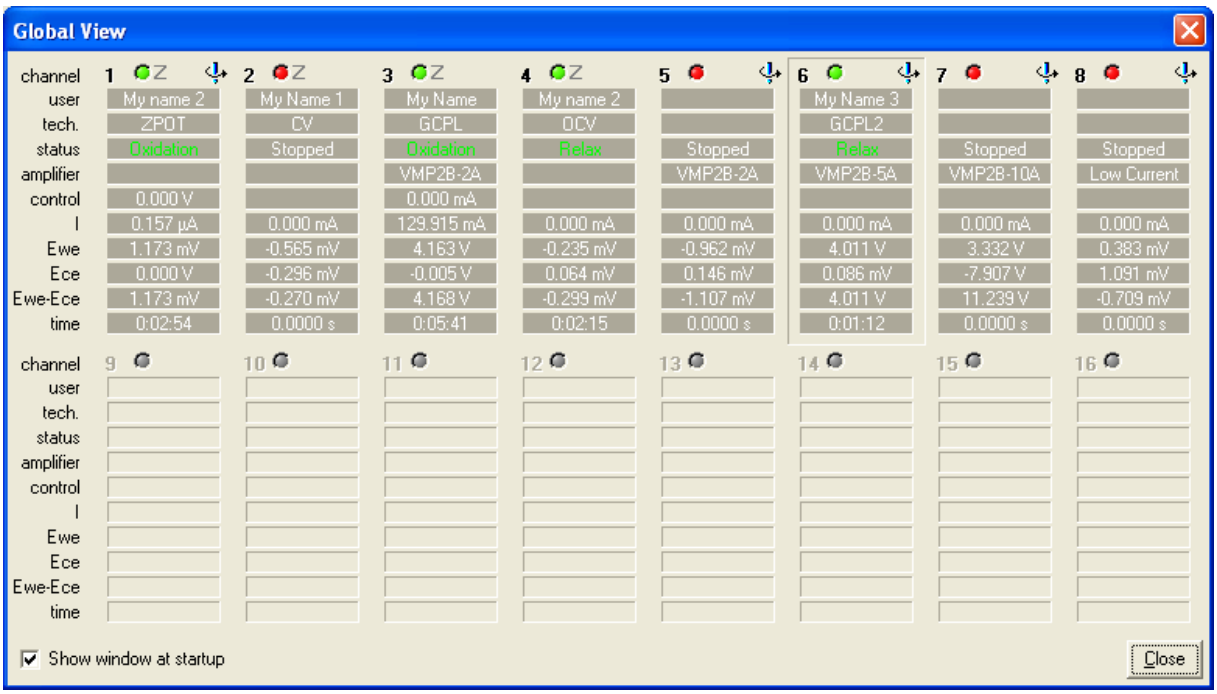

Global View
channel 1 2 3 4 5 6 7 8
user My name 2 My Name 1 My Name My name 2 My Name 3
tech. ZPOT CV GCPL OCV GCPL2
status Oxidation Stopped Oxidation Relax Stopped Relax Stopped Stopped
amplifier VMP2B-2A VMP2B-2A VMP2B-5A VMP2B-10A Low Current
control 0.000 V 0.000 mA
I 0.157 µA 0.000 mA 129.915 mA 0.000 mA 0.000 mA 0.000 mA 0.000 mA 0.000 mA
Ewe 1.173 mV -0.565 mV 4.163 V -0.235 mV -0.962 mV 4.011 V 3.332 V 0.383 mV
Ece 0.000 V -0.296 mV -0.005 V 0.064 mV 0.146 mV 0.086 mV -7.907 V 1.091 mV
Ewe-Ece 1.173 mV -0.270 mV 4.168 V -0.299 mV -1.107 mV 4.011 V 11.239 V -0.709 mV
time 0:02:54 0.0000 s 0:05:41 0:02:15 0.0000 s 0:01:12 0.0000 s 0.0000 s
channel 9 10 11 12 13 14 15 16
user
tech.
status
amplifier
control
I
Ewe
Ece
Ewe-Ece
time
Show window at startup
Close

Fig. 3: “Global view” window.

- When the computer is connected, the global view of the channels shows the following information in standard (according to the configuration of the instrument):

- **channel** number with a **'LED'** - red if there is no experiment running or green color if the channel is running.
- **user** - the channel is available (no username) or is (was) used by another user. Several users can be connected to the instrument, each of the users having one or several channels.

- **tech.** - the experiment type once loaded (e.g. **CV** for Cyclic Voltammetry, **GCPL** for Galvanostatic Cycling with Potential Limitation, **PEIS** for potentio impedance, etc...).
- **status** - the running sequence if an experiment is in progress: **oxidation**, **reduction**, **relax** (open circuit potential), or **stopped**.
- **booster** - the booster type if connected: 1 A, 2 A, 4 A, 5 A, 10 A, 20 A, 80 A, 100 A, a 500 W load or none (for VMP3 technology) or 1 A/48 V (for SP-300 technology).
  - the "p" low current board if connected (for VMP3 technology) or low current cable (for SP-300 technology).

The user has the ability to add several current variables on the global view such as "**Control, I, E_{we}, E_{ce}, E_{we}-E_{ce}** and **time"**. Right click on the channel and select the variable to be hidden/displayed.
You may use **Channels, Global View...** to display the global channel view.

Double clicking on any of the channel window will replace the global view by the specific view of the selected channel.

2.2 Preparing and Running an Experiment with EC-Lab® software

This chapter is designed to guide users through the use of EC-Lab® software.

2.2.1 EC-Lab® main window

Double click on a channel of the global view to select it. You will get the following window:

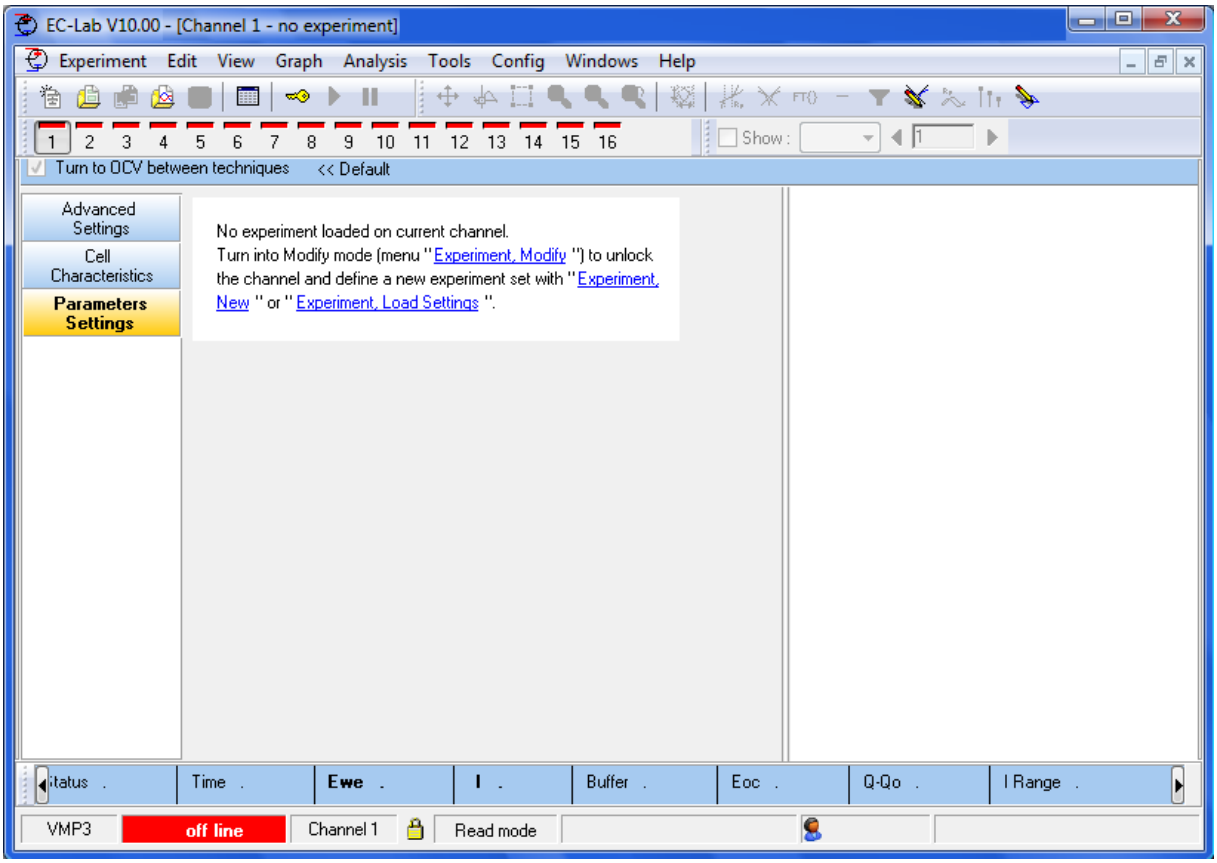

EC-Lab V10.00 - [Channel 1 - no experiment]
Experiment Edit View Graph Analysis Tools Config Windows Help
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Show :
Turn to OCV between techniques
<< Default
Advanced Settings
Cell Characteristics
Parameters Settings
No experiment loaded on current channel.
Turn into Modify mode (menu "Experiment, Modify ") to unlock the channel and define a new experiment set with "Experiment, New " or " Experiment, Load Settings ".
Status
Time
Ewe
I
Buffer
Eoc
Q-Qo
I Range
VMP3
off line
Channel 1
Read mode

Fig. 4: Opening window for experiment setting.

This window shows:

2.2.1.1 Settings tool bar

- At the top:

  - in the blue title bar: the software version with the active channel and the experiment selected
    - the main EC-Lab® bar menu (**Experiment, Edit, View, Graph, Analysis,…, Help**),
    - the settings tool bar with short cut buttons.

Fig. 5: Main tool bar.

The user can change the buttons displayed in the tool bar. To do that, the user can either click on **Config\options\tool bar** and select or deselect the desired buttons (see part 2.9.6, page 52 for more details) or right click with the mouse on the settings tool bar to display the icons selection. The same option is available for the graphics tool bar:

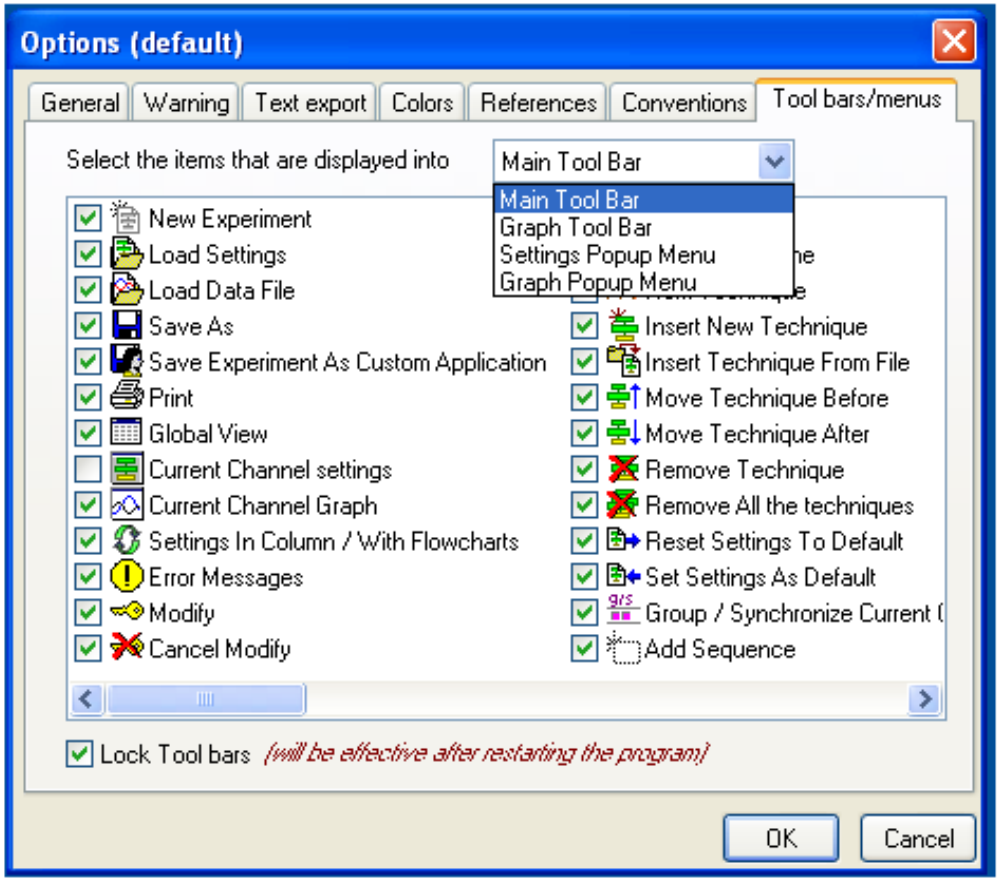


Fig. 6: Main Tool Bar menu to display the icons.

- **Channel tool bar with buttons 1 to 16** (depending on the instrument and on the number of channels that can be inserted into the chassis).

Fig. 7: Channel selection tool bar.

It allows the user to select the current channel(s). Clicking on one of the buttons enables the user to see the channel status. The corresponding "lights" give the on/off status of the channels: red if there is no experiment running or green if the channel is running.

2.2.1.2 The graphic tool bars

- The graphics tool bar with short cut buttons (including zoom, rescale, analyses, and graph properties). Report to the graphics tools part for more details.

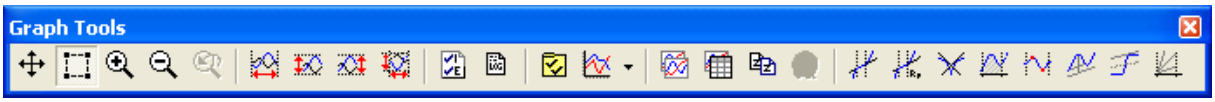


Fig. 8: Graphic tool bar.

- The fast graphic selection tool bar with choice of the displayed cycle:

Fig. 9: Fast Graph selection tool bar.

2.2.1.3 Status tool bar

- <u>At the bottom:</u> the status tool bar shows:

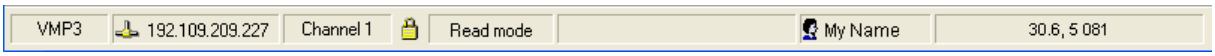


Fig. 10: Status tool bar.

- the connected device: SP-150, SP-300, SP-200, VMP 16/20 (16 channels and 20 ms acquisition rate), VMP2, VMP3, VSP, MPG or BiStat,
- the instrument's IP (internet protocol) address if the instrument is connected to the computer through an Ethernet connection or USB for an USB connection,
- the selected channel,
- a lock showing the Modify/Accept mode in relation with the box near: "Read mode" or "Modify mode",
- the remote status (receive or disconnected),
- the user name,
- the mouse coordinates on the graphic display.

2.2.1.4 Current values tool bar

- <u>On the left side or in the bottom</u>: a tool bar shows the current values of the electrochemical cell connected to the channel:

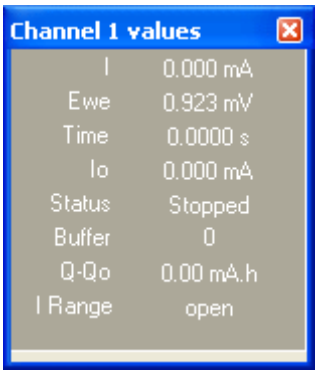


Fig. 11: Current values tool bar.

- **Current**, $\mathbf{E_{we}}$ and **Time** are the current, the working electrode potential and the time from the beginning of the experiment,
- $\mathbf{I_0}$ (or $\mathbf{E_0}$). $\mathbf{I_0}$ is the initial current value obtained just after a potential step in potentiodynamic mode. $\mathbf{E_{oc}}$ is the potential value reached at the end of the previous open circuit period,
- **Status** gives the nature of the running sequence: **oxidation**, **reduction**, **relax** (open circuit, measuring the potential), **paused** or **stopped**. Buffer full will be displayed in the case where the instrument's intermediate buffer is full (saturated network...),
- **Buffer** indicates the buffer filling level,
- $\mathbf{Q - Q_0}$ is the total charge since the beginning of the experiment,
- **The current range,**
- $\mathbf{N_s}$ is the number of the current sequence,
- $\mathbf{n_c}$ is the number of the current cycle or loop.

Note: Two protocols (Batteries: GCPL and PCGA) propose an additional display variable **$\mathbf{X - X_0}$.**

This toolbar can be unlocked with the mouse and set as a linear bar locked to the status bar at bottom of EC-Lab® window or to the graphic bar at the top of the window.

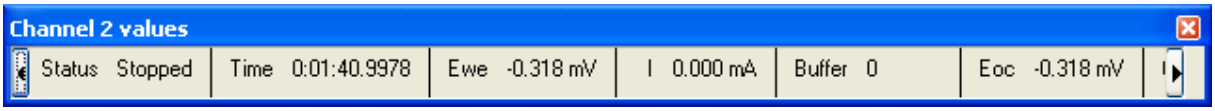


Fig. 12: Current values tool bar in a linear format.

Note: In the default configuration, all the tool bars are locked in their position. But at the user's convenience tool bars can be moved to other places in the window. To do so, click on **Config\Option\Tool bars** and deactivate the "**Lock tool bar**" box. This will be effective after restarting the software. Once the user has defined a new configuration of the tool bars he can relock the tool bar the same way he unlocked.
Note also that some of the current values can be "highlighted in bold. In the config/option/colors menu.

2.2.1.5 The parameter settings frame

- Below in the middle:

The default window displayed when EC-Lab® is launched is the “Parameter Settings” window. Three buttons permit the user to switch between three windows associated to the protocol: the "Advanced Settings", the "Cell Characteristics" and the "Parameter Settings".

When no technique or application is loaded in the settings window, a small text is displayed indicating how to proceed:

“No experiment loaded on current channel.
Turn into modify mode (menu “Experiment/Modify”) to unlock the channel and define a new experiment set with “Experiment/New” or “Experiment/Load setting”

A white column and a blue row are displayed:

- The column will contain the techniques of a linked experiment. The settings of each technique will be available by clicking on the technique’s icon.
- The “Turn to OCV between techniques” option offers the possibility to add an OCV period between linked techniques.

Fig. 13: Row in the parameter settings window showing advanced parameters.

2.2.1.6 Right click on the “Parameter settings” window

EC-Lab® software contains a context menu. Right click on the main EC-Lab® window to display all the commands available on the mouse right click. Commands on the mouse right click depend on the displayed window. Other commands are available with the mouse right click on the graphic display.

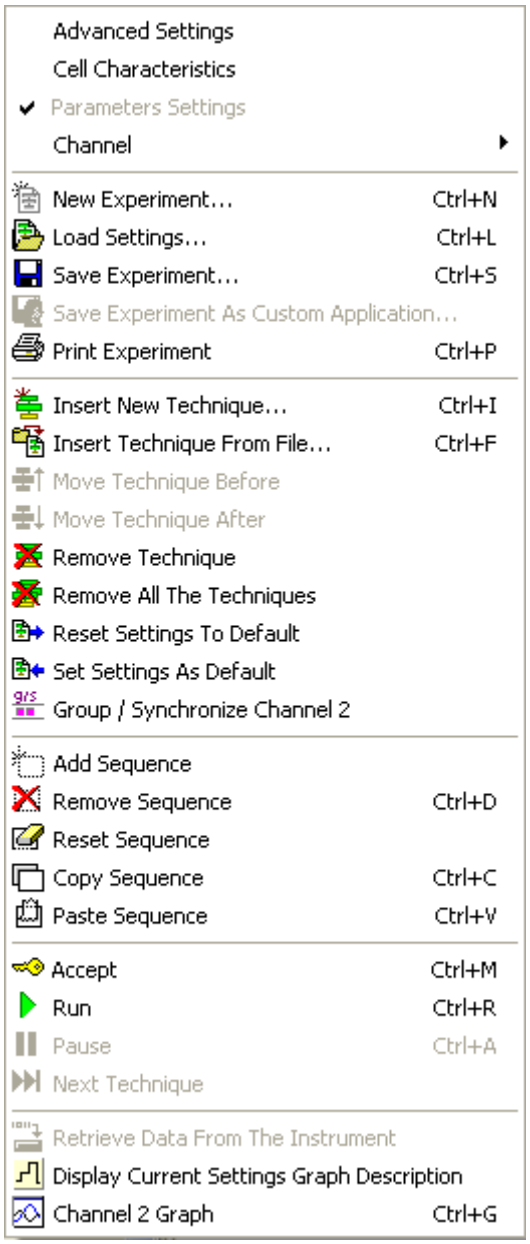


Fig. 14: Mouse Right Click on the main window of EC-Lab® software.

Most of the commands are available with the right click. They are separated into 6 frames. The first frame concerns the available setting tabs, the second one is for the experiment from building to printing. The third frame is for the modification of an experiment and creation of linked experiments. The fourth one is devoted to sequences (addition, removing) and the fifth one controls the run. The last one is dedicated to the different view.

2.2.2 The bar menu

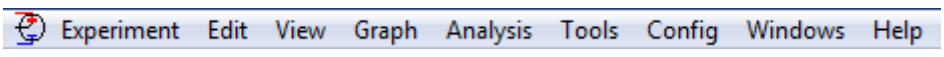


Fig. 15: The bar menu of EC-Lab® software main window.

The bar menu has been designed in such a way that it follows an increasing progression in the experiment from the experiment definition to the curves analysis. Each menu is described below.

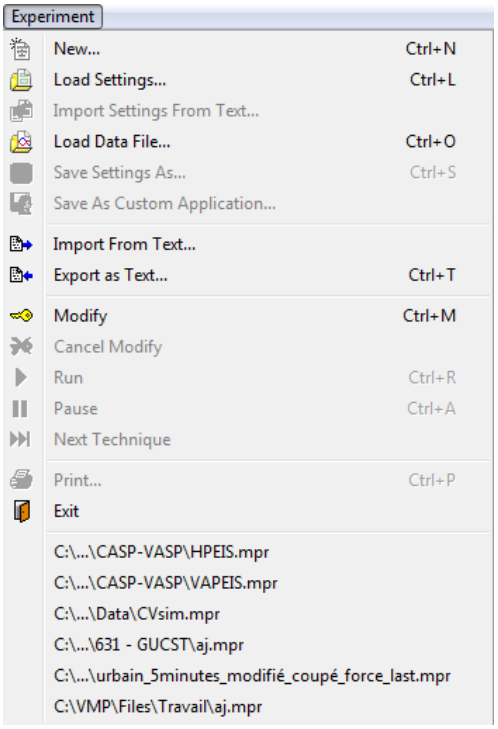


Fig. 16: Experiment Menu.

This menu allows the user to build a new experiment and load an existing setting file or an existing data file made with our potentiostat or another one. Our software is able to read other manufacturer formats.
Saving options are also available.
The second frame offers the user the possibility to import a text data file from another manufacturer when it is not possible to open it directly.
Experiment commands (**Modify**, **run**, **Pause** and **next technique**) are in the third frame. **Print** and **Exit** commands can be found in the fourth frame.
In the last frame the last opened files are listed.

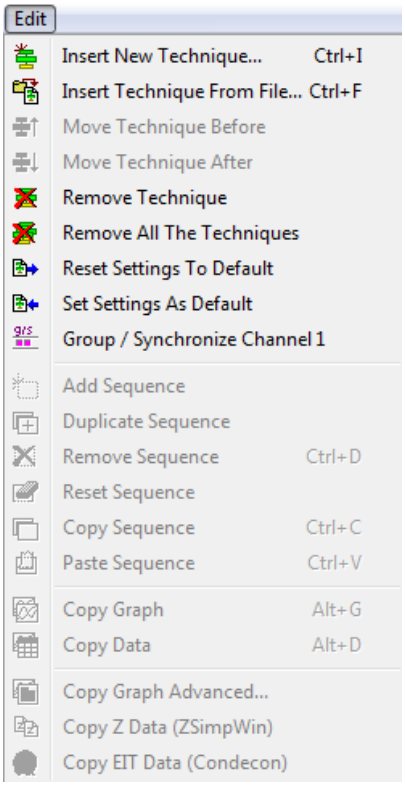


Fig. 17: Edit Menu.

The "Edit" menu concerns building an experiment, insertion (move up or move down), or removing techniques from a setting already loaded in the parameter settings window. A Group and synchronize window is also available in this menu. The second frame is for sequence addition or removal from a technique (when this is possible), and the two last ones offer copy options (Graph, Data, ZSimpWin format) on the graphic display.

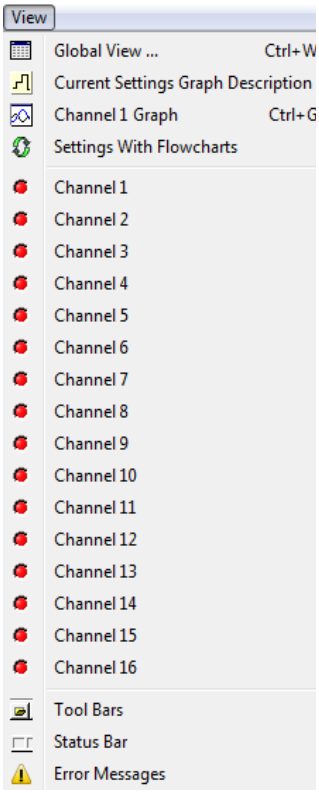


Fig. 18: View Menu.

This menu is for the Settings or Graph display and to select a channel. In the last frame, tool bars or error messages can be displayed.

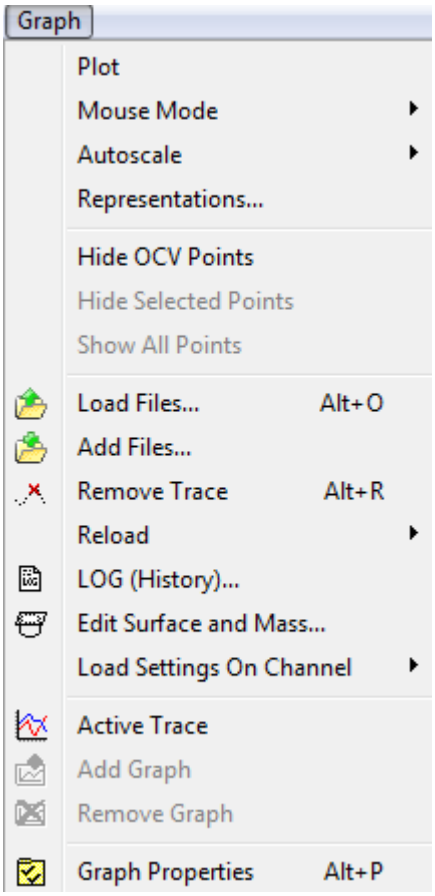


Fig. 19: Graph Menu.

This menu includes all the graph tools (zoom in and out, point selection, auto scale, selection and graph properties) and the graph representation menu. This menu allows the user to load or add new files to the graph.

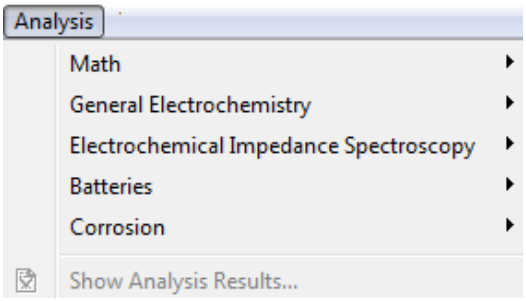


Fig. 20: Analysis Menu

The analysis menu contains various Analysis techniques. These analysis tools are grouped depending of the application: general electrochemistry, EIS, batteries and corrosion.

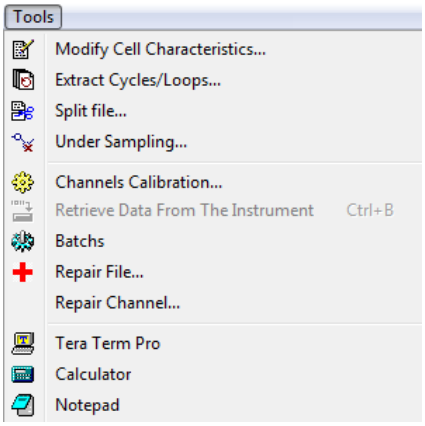


Fig. 21: Tools Menu.

The tools menu is made of three frames. The first one is for the data file (modify cell characteristics, export as or import from text, split, under sample, repair file). The second one is for the channels (calibration, repair channel). The last one concern tools such as Tera Term Pro (used to change the instrument configuration) calculator and Notepad.

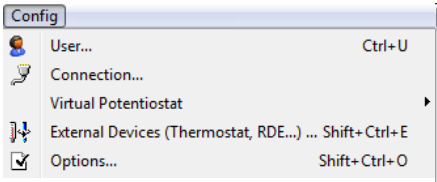


Fig. 22: Config Menu.

The config menu is dedicated to instrument and software configuration (define the user name, connect the instrument, configure an external device, software display options). The virtual potentiostat option is available only when the computer is not connected to the instrument (off line).

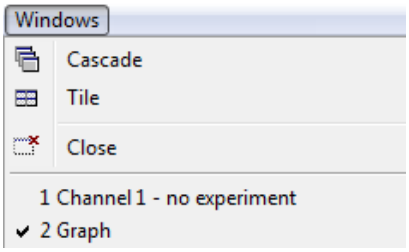


Fig. 23: Windows Menu.

This menu is used to display and select windows.

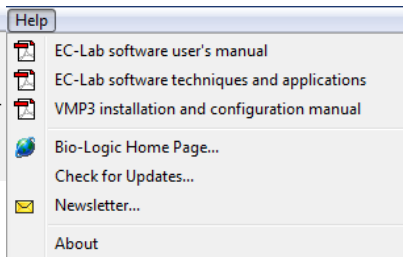


Fig. 24: Help Menu.

The help menu contains pdf files of the software manual, the instrument installation and configuration manual and several quickstarts. This menu provides also a direct link to the Bio-Logic website and a way to check for software updates . It is also possible to access to the Newsletter (this Newsletter is also automatically displayed when the software is installed for the first time on the computer and for each upgrade).

2.2.3 Selecting a technique

First select a channel on the channel bar. There are three different options for loading a new experiment.

1-Click on the **Modify** button then the **Accept** button activates . Then click on the “New experiment” button .
2-Click on the blue “New Experiment” link on the parameter settings window.
3-The user can also click on the right button of the mouse and select “New experiment” in the menu.

Note: - It is not always necessary to click on the “Modify” button before selecting a command. The software is able to switch to the “modify” mode when the user wants to change the setting parameters. In that case the following message is displayed:
- When double clicking on a channel belonging to another user, a warning message is displayed, asking for confirmation of the user's name modification.

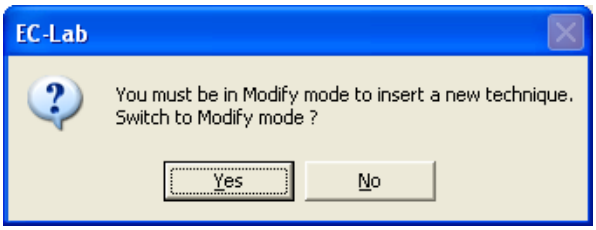


Fig. 25: Message displayed before to switch in Modify mode.

Click on Yes and the "**Insert Techniques"** window will appear with the different techniques available with EC-Lab® software.

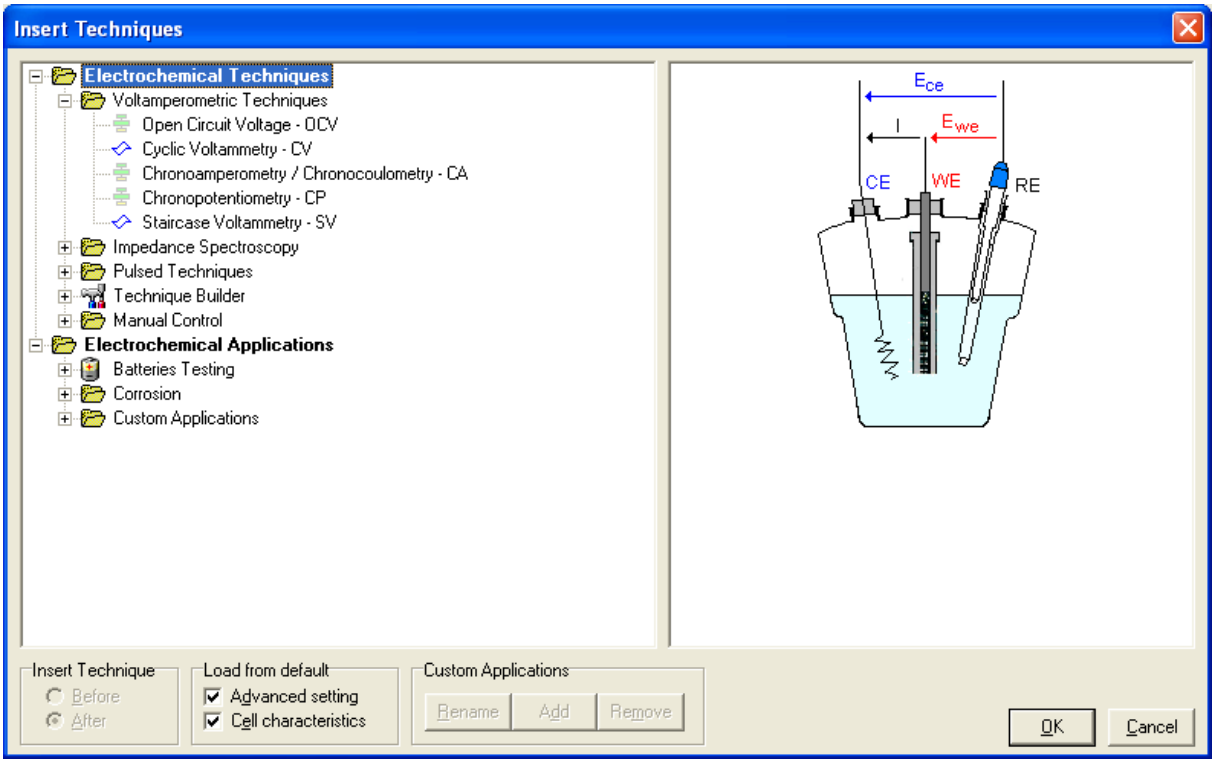


Fig. 26: Techniques selection window.

Techniques available with EC-Lab® software have been separated into two different fields: *Electrochemical Techniques* and *Electrochemical Applications*. Electrochemical techniques include voltamperometric techniques, electrochemical impedance spectroscopy, pulsed techniques, a tool to build complex experiments, manual control and also an ohmic drop determination techniques by EIS measurements. Electrochemical Applications include battery testing, corrosion measurement, custom applications and special applications.
At the bottom of this window different options can be selected when a protocol is loaded. In the case of linked techniques, the user can insert the technique either before or after the technique already loaded in the parameter settings window. This option will be described in detail in the linked technique section. The technique can be loaded with or without the "Cell characteristics" and the "Advanced Settings" of the default setting file. The user has now the possibility to create and save his own experiment as a custom application (see custom application section).

For example, choose the cyclic voltammetry technique and click **OK** or double click. On the right frame, a picture and description is available for each protocol.

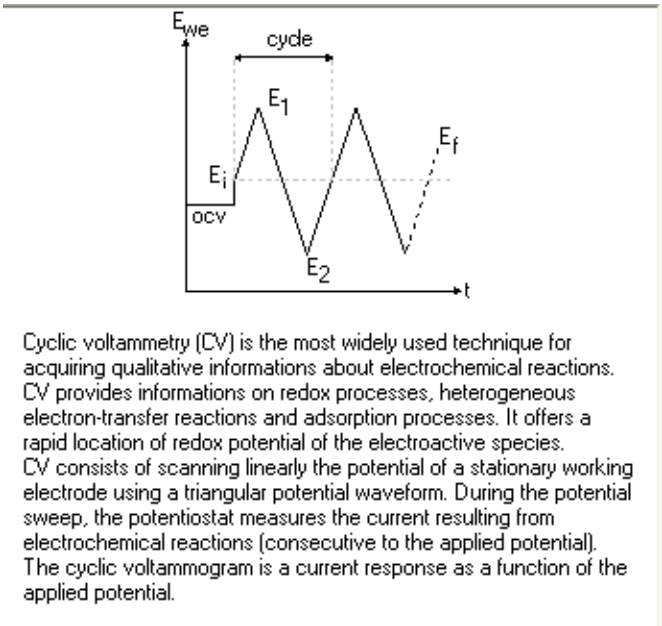

E we
cycle
E1
Ef
Ei
ocv
E2
t
Cyclic voltammetry (CV) is the most widely used technique for acquiring qualitative informations about electrochemical reactions. CV provides informations on redox processes, heterogeneous electron-transfer reactions and adsorption processes. It offers a rapid location of redox potential of the electroactive species.
CV consists of scanning linearly the potential of a stationary working electrode using a triangular potential waveform. During the potential sweep, the potentiostat measures the current resulting from electrochemical reactions (consecutive to the applied potential).
The cyclic voltammogram is a current response as a function of the applied potential.

Fig. 27: CV technique picture and description on the experiment window.

2.2.4 Parameter Settings

When a technique is selected the default open window is the "Setting Parameters" window. The user must type the experiment parameters into the boxes of the blocks.

Two ways are available to display a technique:

- the detailed flow-diagram (Fig. 28) and its table,
- the detailed column-diagram (Fig. 29).

It is possible to switch between the two displaying modes with the button.

Setting parameters can also be done using selected settings files from user's previous experiment files.

Click on the **Load Settings** icon then select an .mps setting file or a previous .mpr raw file corresponding to the selected technique and click **OK**. You can right click on the mouse and select "Load settings…".

Note: Most of the techniques allows the user to add sequences of the same techniques using mouse right click or using the Edit menu.

On the "**Parameters Settings**" tab the CV detailed flow diagram or the column diagram is display:

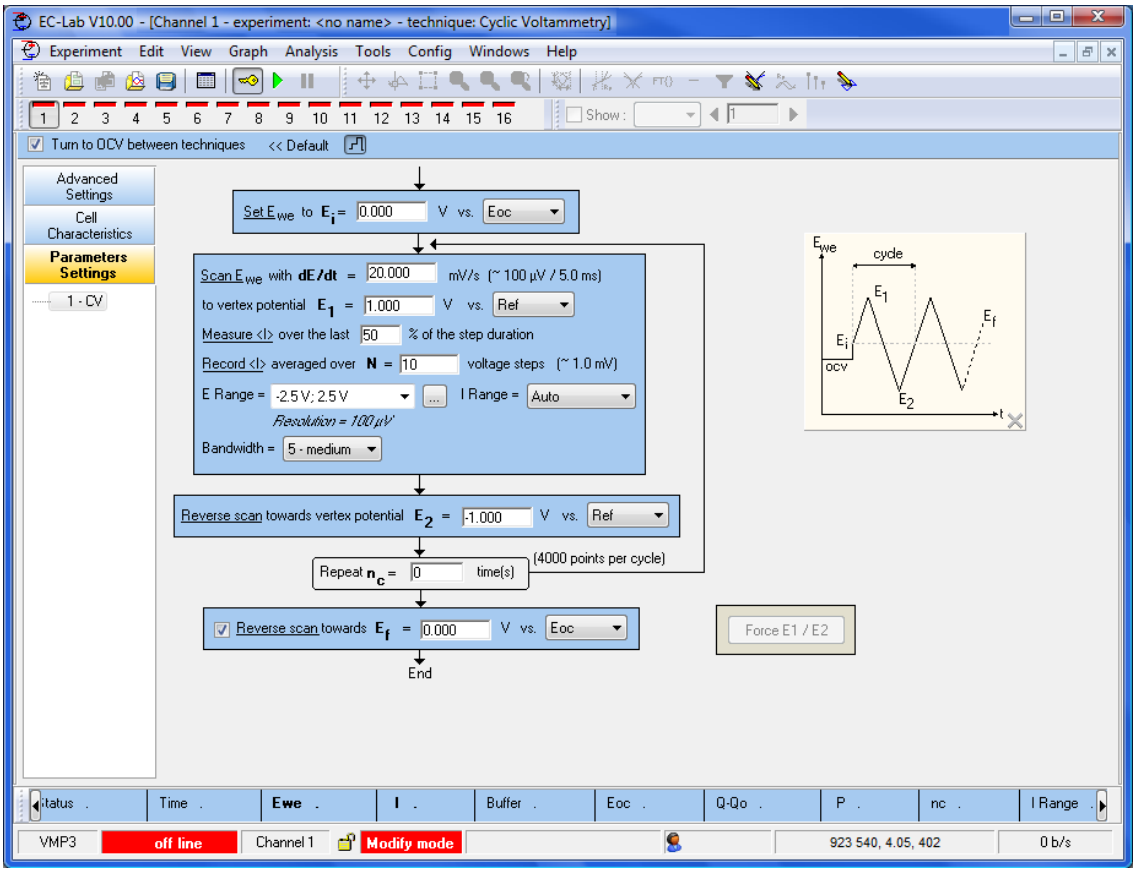


Fig. 28: Cyclic Voltammetry detailed flow diagram.

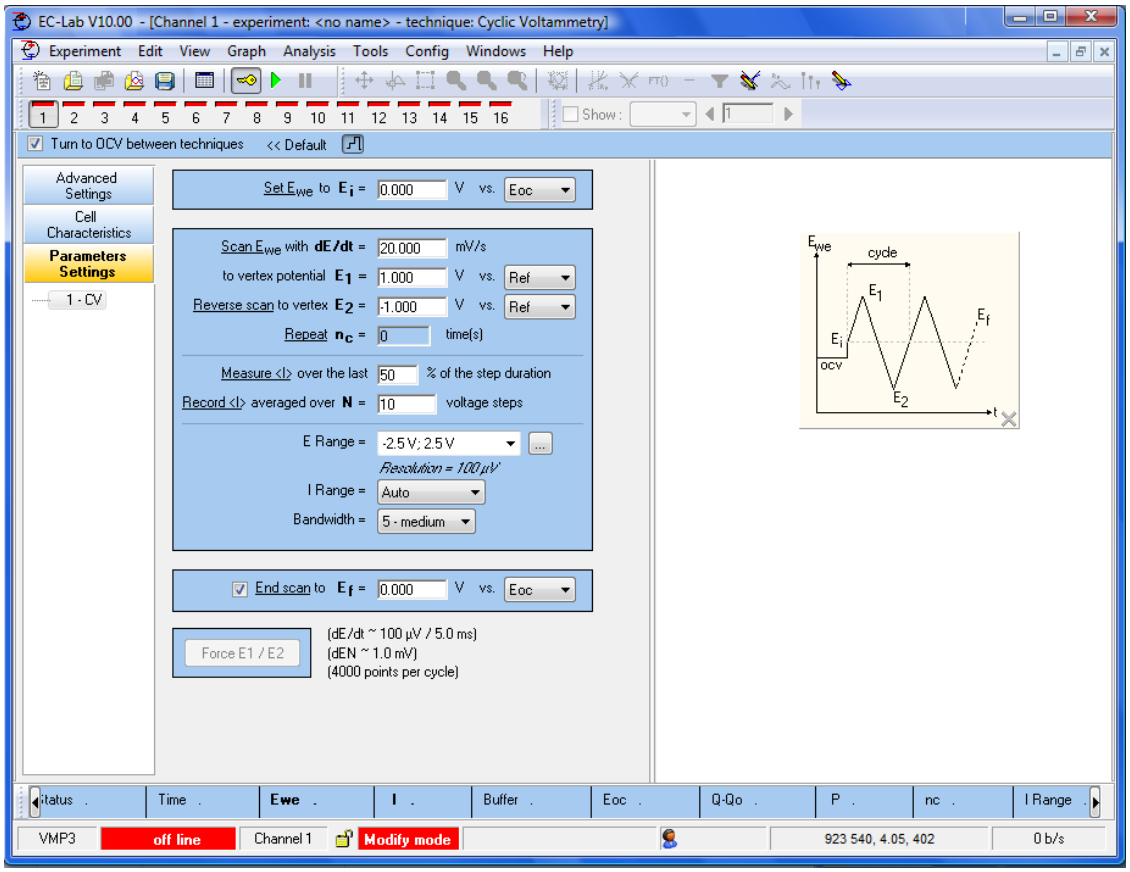


Fig. 29: Cyclic Voltammetry detailed column diagram.

When a technique is loaded on a channel, the detailed flow diagram is displayed. In the blue column, the icon shows the loaded technique, and in the blue row, the user can adjust the potential control resolution (here to 100 µV, for more details about the potential control resolution refer to section 5.2.1 page 166). Moreover, on the right of this row, a button is available to show the graphic describing the technique and its variables.

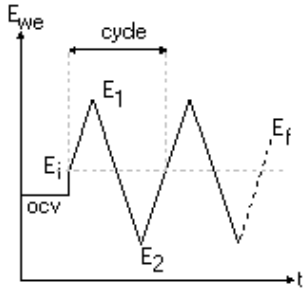


Fig. 30: CV graphic description.

The EC-Lab® software protocols are made of blocks. Each one is dedicated to a particular function. When not activated, a block is in gray color. The user has to set parameters in the boxes to activate a block, which becomes colored (color for the repeat block is different when activated). A box with an active value is white and stays colored when not activated.

The recording function "Record" in the first block can be used with either dE_R or with dt_R resolution or with both. Data recording with dE_R resolution reduces the number of experimental points without loosing any "interesting" changes in potential. When there is no potential change, only points according to the dt_R value are recorded but if there is a sharp peak in potential, the rate of recording increases.

In every technique with potential control the user can now choose the current recording conditions between an averaged value (per potential step for a sweep) and an instantaneous value every dt (see the application section).

When a technique is loaded in the parameter settings window, a small icon is displayed on the left of the flow diagram with the name of the technique and the number (level) in the experiment (in case of linked experiments). During a run, this icon is circled with a green frame.

Notes:

- E Range adjustment
On the technique the user can define the potential range (min and max values) to increase to potential resolution from 305 µV (333 µV for SP-300 and SP-200) to up to 5 µV.

- Scan rate setting
When entering the potential scan rate in mV/s the default choice of the system proposes a scan rate, as close as possible to the requested one and obtained with the smallest possible step amplitude.
The scan rate is defined by dE/dt.

- I Range
The current range has to be fixed by the user. When the current is a measured value, I measured can be greater than the chosen I Range without "current overflow" error message. In this case the potential range is reduced to ± 9 V instead of ± 10 V. The maximum measurable current is 2.4*I Range. For example with I Range = 10 mA, the current measured can be 24 mA with a potential range ± 9 V. The same thing is possible when the current is controlled (For more details about that, please see section 5.2.1 page 166).

Note: with booster ranges and 1 A range of SP-300 and SP-200, this relationship is not available.

- Bandwidth

The VMP2/Z, VMP3, VSP, MPG2, SP-150, HCP-803, HCP-1005 and BiStat devices propose a choice of 7 bandwidths ("damping factors"), 8 for the VMP and MPG devices and 9 for SP-300 and SP-200 devices in the regulation loop of the potentiostat. The frequency bandwidth depends on the cell impedance and the user should test filtering effect on his experiment before choosing the damping factor.

The following table gives typical frequency bandwidths of the control amplifiers poles for the VMP3, VSP, MPG2, SP-150, HCP-803, VMP2, and BiStat:

Bandwidth	**7**	**6**	**5**	**4**	**3**	**2**	**1**
Frequency	680 kHz	217 kHz	62 kHz	21 kHz	3.2 kHz	318 Hz	32 Hz

The following table gives typical frequency bandwidths obtained with a 2 kΩ resistor connected between the working electrode and the reference electrode coupled with the counter electrode (2 points connection) for the VMP and MPG.

Bandwidth	**8**	**7**	**6**	**5**	**4**	**3**	**2**	**1**
Frequency	2 MHz	600 kHz	200 kHz	60 kHz	20 kHz	6 kHz	2 kHz	600 Hz

Note: refer to the SP-300 or SP-200 installation and configuration manual for details about bandwidth definition for SP-300 and SP-200 instruments.

When the mouse pointer stands for several seconds on a box a hint appears. The hint is a visual control text that gives the user information about the box. It shows the min and the max values of the variable as well as the value that cancels the box.

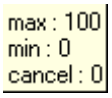


Fig. 31: Hint.

For several protocols in the flow diagram mode, a table appears automatically. It allows the user to make an experiment with several sequences (different parameters) that will be executed one after the other. N_s defines the sequences of the protocol. One row of the table is a sequence of the experiment. The experiment parameters can be reached and modified in the table cells as well as in the flow diagram of the parameter settings window.

Ns	tR (h:m:s)	dER/dt (mV/h)	dER (mV)	dtR (s)	Ei (V)	vs.	ti (h:m:s)	IM	unit IM
0	0:00:2.0000	0.0	0.00	1.0000	0.350	<None>	0:00:10.0000	0.000	mA
1	0:01:0.0000	0.0	0.00	0.1000	0.300	<None>	0:01:0.0000	0.000	mA
2	0:00:1.0000	0.0	0.00	0.1000	-0.300	<None>	0:01:0.0000	0.000	mA
3									

Fig. 32: EC-Lab® table.

During the run, the active row of the table (sequence running) appears in color. The default number of rows is 10. But the user can insert, delete, append, copy, and paste up to 99 rows by clicking the right button of the mouse. It can be a very interesting tool when the user wants to repeat an experiment with one different parameter in a sequence. It is also possible to cut, copy and paste only one cell of the table.

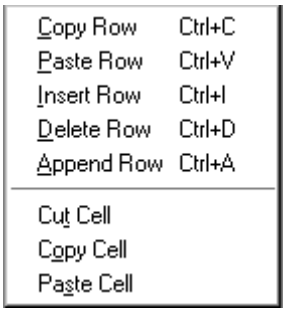


Fig. 33: Table right click with the mouse.

Note:

- The user can define different current ranges for each sequence if an OCV period separates the sequences (at the beginning of each sequence for example).
- It is possible to repeat a block in a sequence (goto sequence N_s').

2.2.5 Cell characteristics

Clicking on the "**Cell Characteristics**" tab will display the cell characteristics window:

2.2.5.1 Standard "Cell Characteristics" window

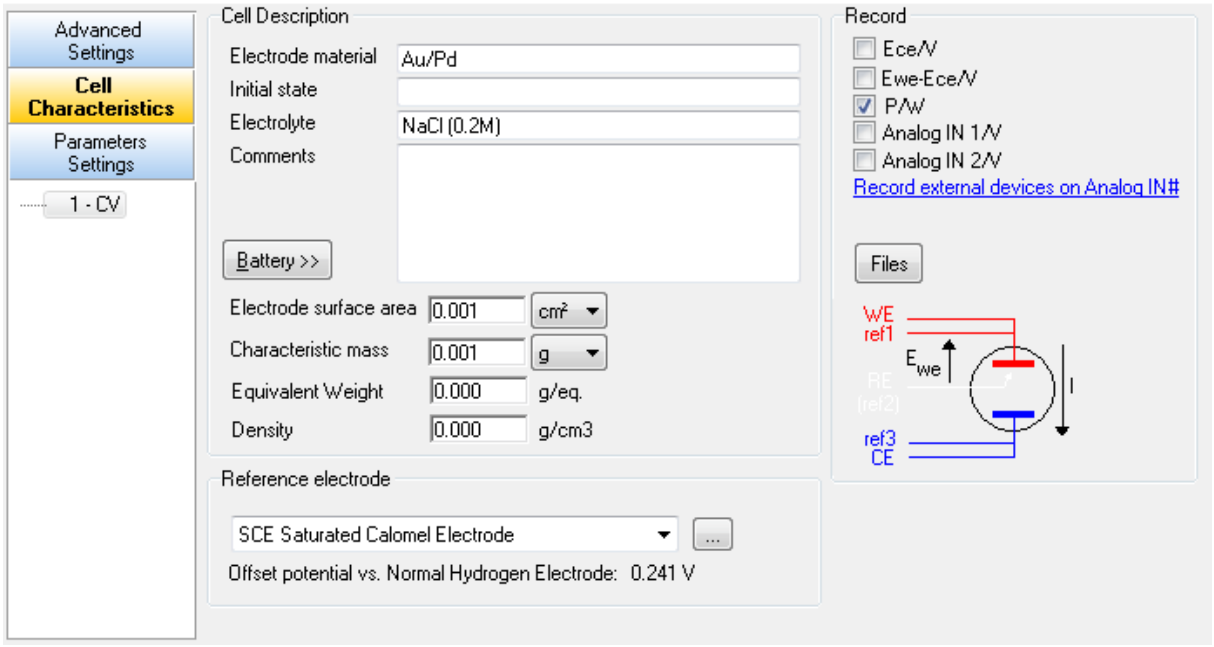


Fig. 34: Cell characteristics window for a Cyclic Voltammetry experiment.

You can either fill blank boxes, entering comments and values, or load them from a **.mps** setting file or a **.mpr** raw file using **Load Setting...** on the right click menu.

This window allows the user to:

- add information about the electrochemical cell (material, initial state, electrolyte and comments),
- set the electrode surface area, the characteristic mass, the equivalent weight and the density of the studied material. When defined these parameters are automatically used to

calculate the corrosion rate after a Tafel Fit. They are also used for the density plot. To modify the electrode surface area or characteristic mass, select "**Edit surface and mass**" in the Graph menu. Then the window below appears,

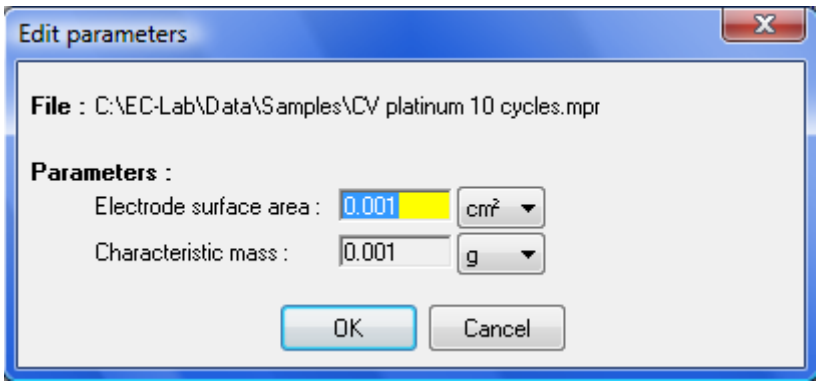


Fig. 35: Edit surface and mass window.

- set the reference electrode used in the experiment (either chosen in the list or added while clicking on the corresponding tab),
- record the counter electrode potential (E_{ce}),
- calculate E_{we}-E_{ce}/V and store the values into the data file,
- record the power (E_{we}*I) calculated in the instrument,
- record external signals (pH, T, P,...) using auxiliary inputs 1 (Analog In1) and 2 (Analog In2),
- access the external device configuration window using the link in blue.

2.2.5.2 Cell characteristic window in column format

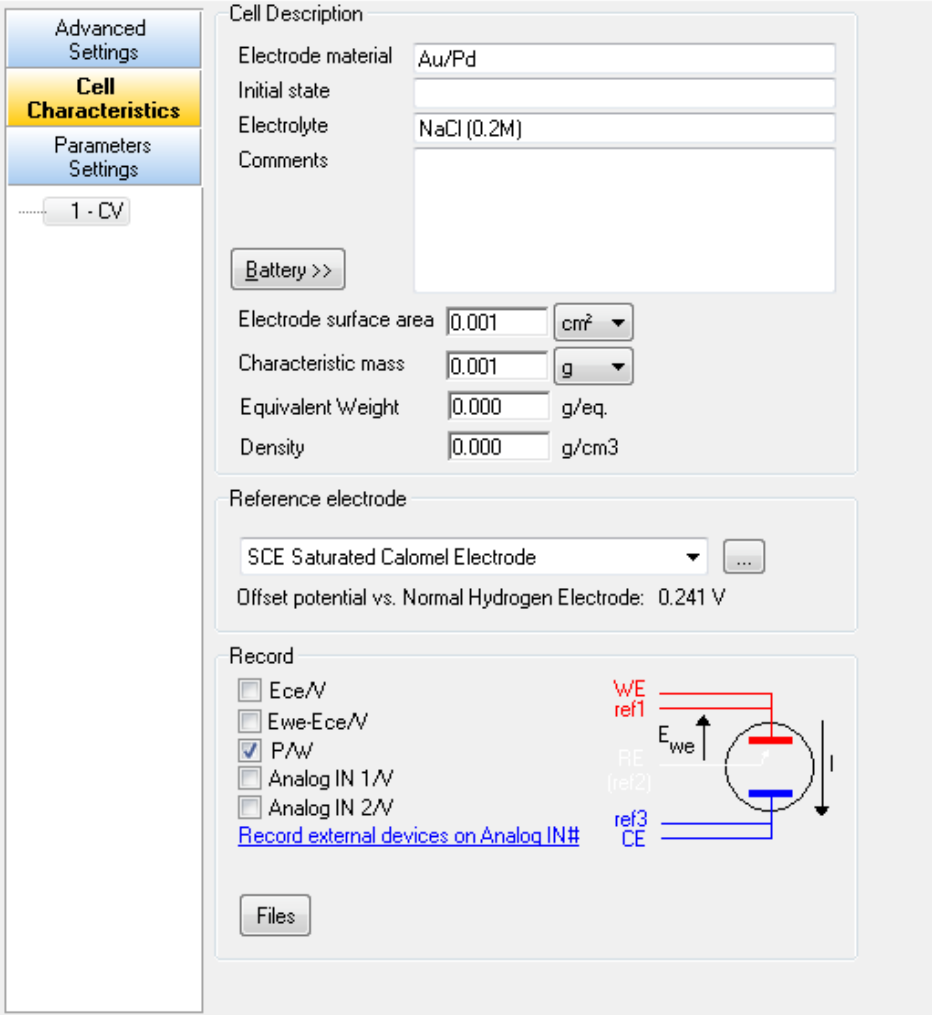


Fig. 36: Cell characteristic window in column format.

2.2.5.3 Battery "Cell Characteristics" window

Two other buttons are available in this window: **Battery** and **Files**. The battery cell characteristics are automatically displayed when a battery testing setting file is loaded. The corresponding window is as follows:

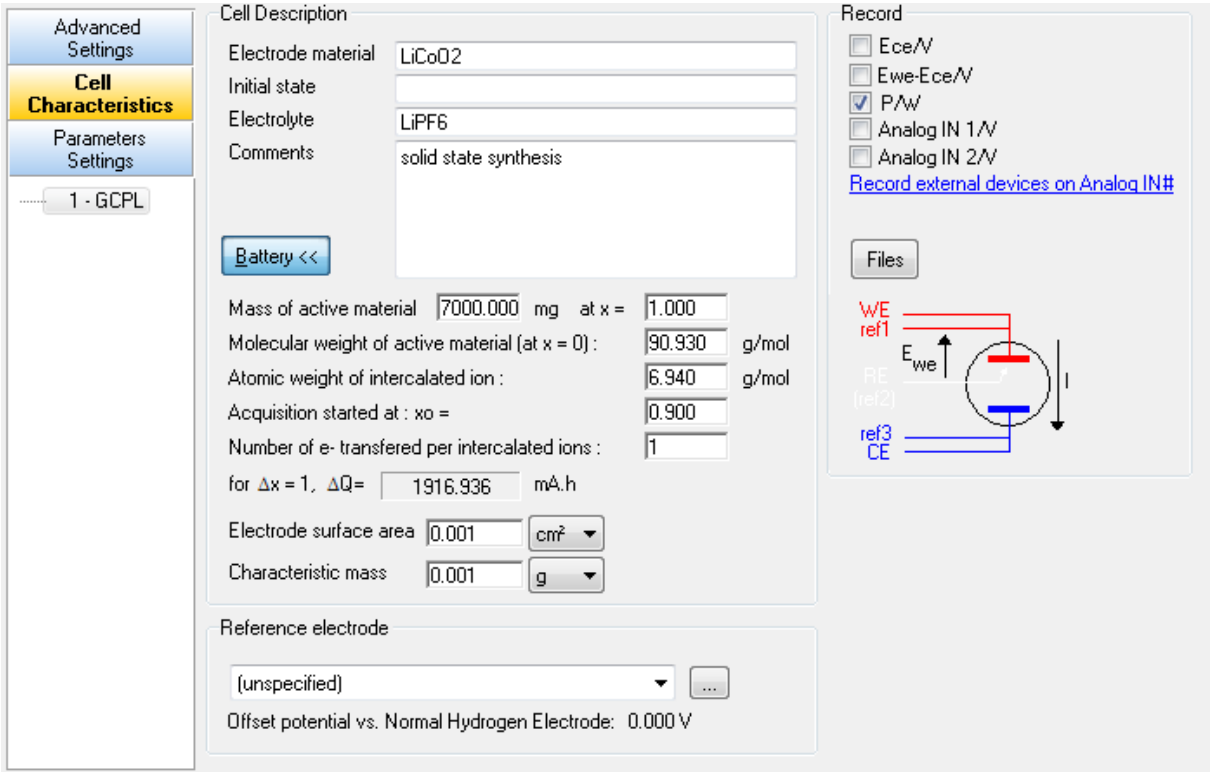


Fig. 37: Cell characteristics window for a battery experiment.

This window offers the following possibilities to the user:

- add information about the electrochemical cell (material, initial state, electrolyte and comments),
- This window has been designed for battery electrode materials acting as intercalation electrode, which is the case of several primary and secondary batteries. It allows you to enter the physical characteristics corresponding to the active material of the working electrode. This makes on-line monitoring of the redox processes possible in term of normalized units (molar amounts of intercalation). The mass “m” of active material in the cell has to be set with a given intercalation rate (for example Xf = 1 for $LiCoO_2$). The molecular weight of the active material does not include the intercalated ion for which the atomic weight is set in a separate box. For the example of $LiCoO_2$ above, the molecular weight of CoO_2 is 90.93 $g.mol^{-1}$ and the atomic weight of the intercalated ion Li is 6.94 $g.mol^{-1}$. The user also has to define the intercalation rate x0 when the acquisition starts and the number of electron “ne” transferred par intercalated ion.

$$x = xo - (Q - Qo) \times \frac{(molecular\ weight + xf \times atomic\ weight)}{(ne \times mass \times 0.001 \times F)}$$

  With all the parameters, the charge variation ΔQ=Q-Qo is calculated for Δx=x-xo=1.
- The electrode surface area and the characteristic mass can be added.
- set the reference electrode used in the experiment (either chosen in the list or added while clicking on the corresponding tab),
- record the counter electrode potential (E_{ce}),
- calculate E_{we}-E_{ce}/V and store the values into the data file,
- record the power (E_{we}*I) calculated in the instrument,
- record external signals (pH, T, P,...) using auxiliary inputs 1 (Analog In1) and 2 (Analog In2),
- access the external device configuration window using the link in blue.

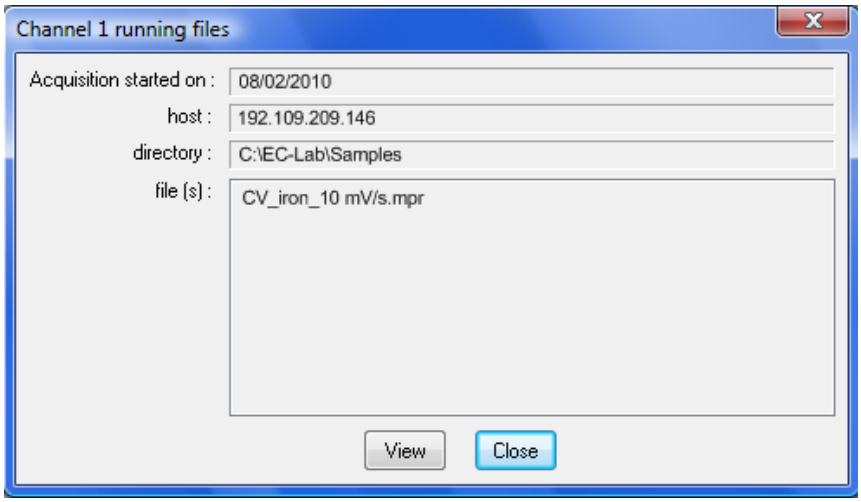


Fig. 38: Cell characteristics Files window.

All boxes (Acquisition started on, host, directory and file) are filled automatically when the experiment is started.

2.2.6 Advanced Settings

The advanced settings window includes several parameters that can be adjusted on the instrument. These parameters such as compliance, the electrodes connection, experiment limits, and the smooth option are used in specific experiments.
Depending of the instrument of the Bio-Logic range used, various “Advanced Settings” windows are available, examples of these windows are given in the following figures.
To change the values, click on the **Modify** button, enter the new settings, and click on the **Accept** button to send the new settings to the instrument.

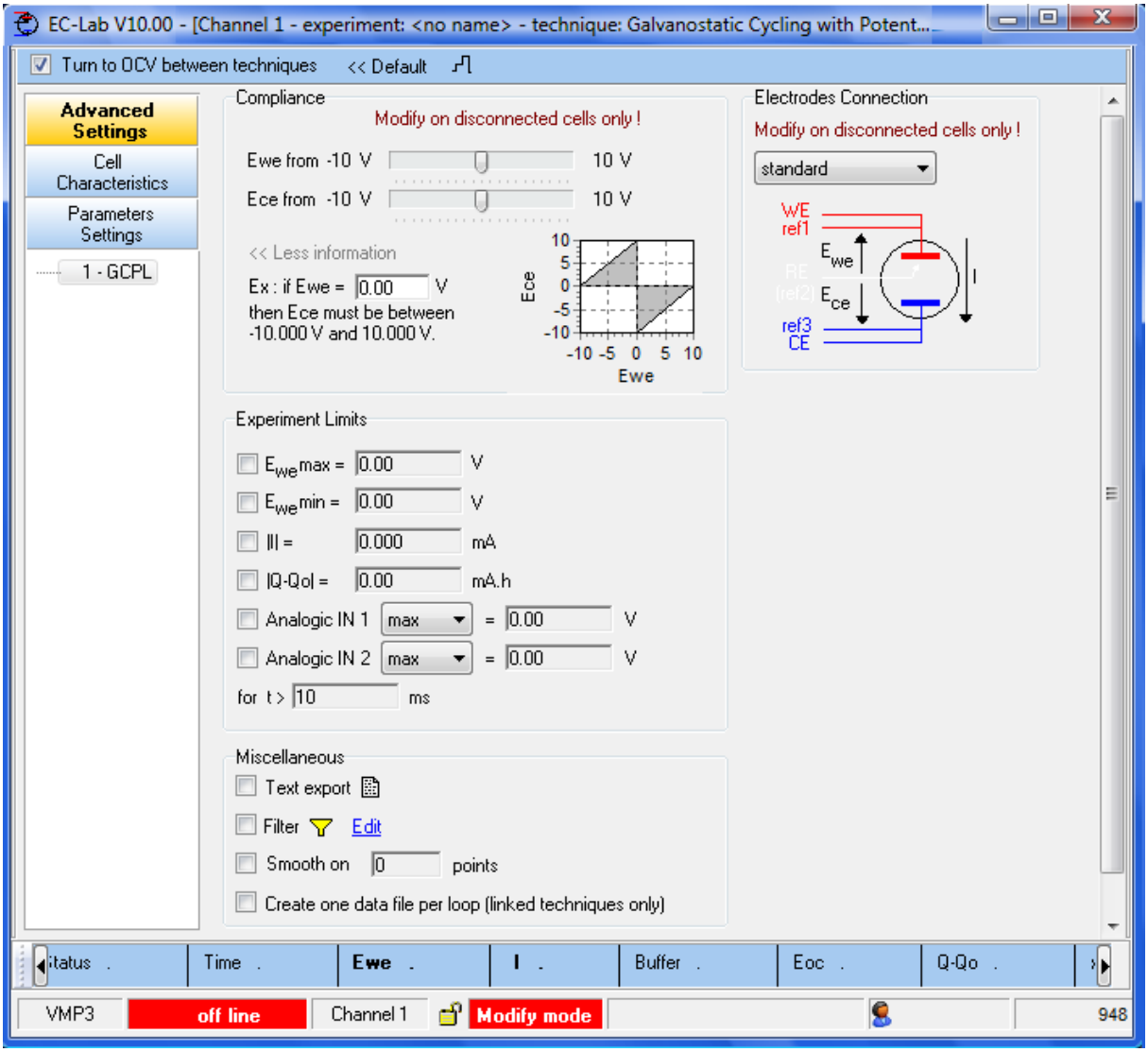


Fig. 39: Advanced settings window for VMP3, SP-150, VSP instruments.

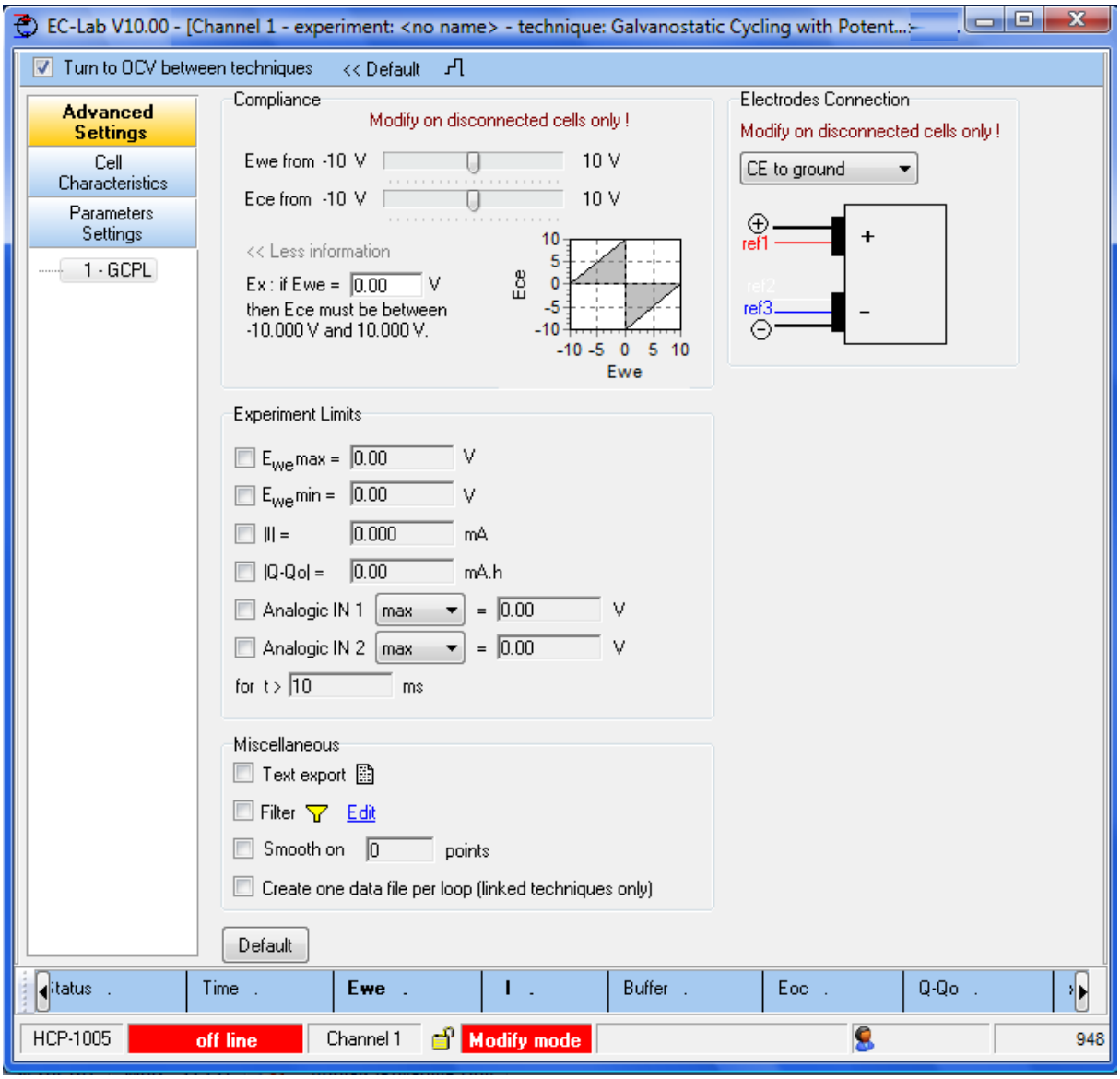


Fig. 40: Advanced settings window for HCP-1005 instrument.

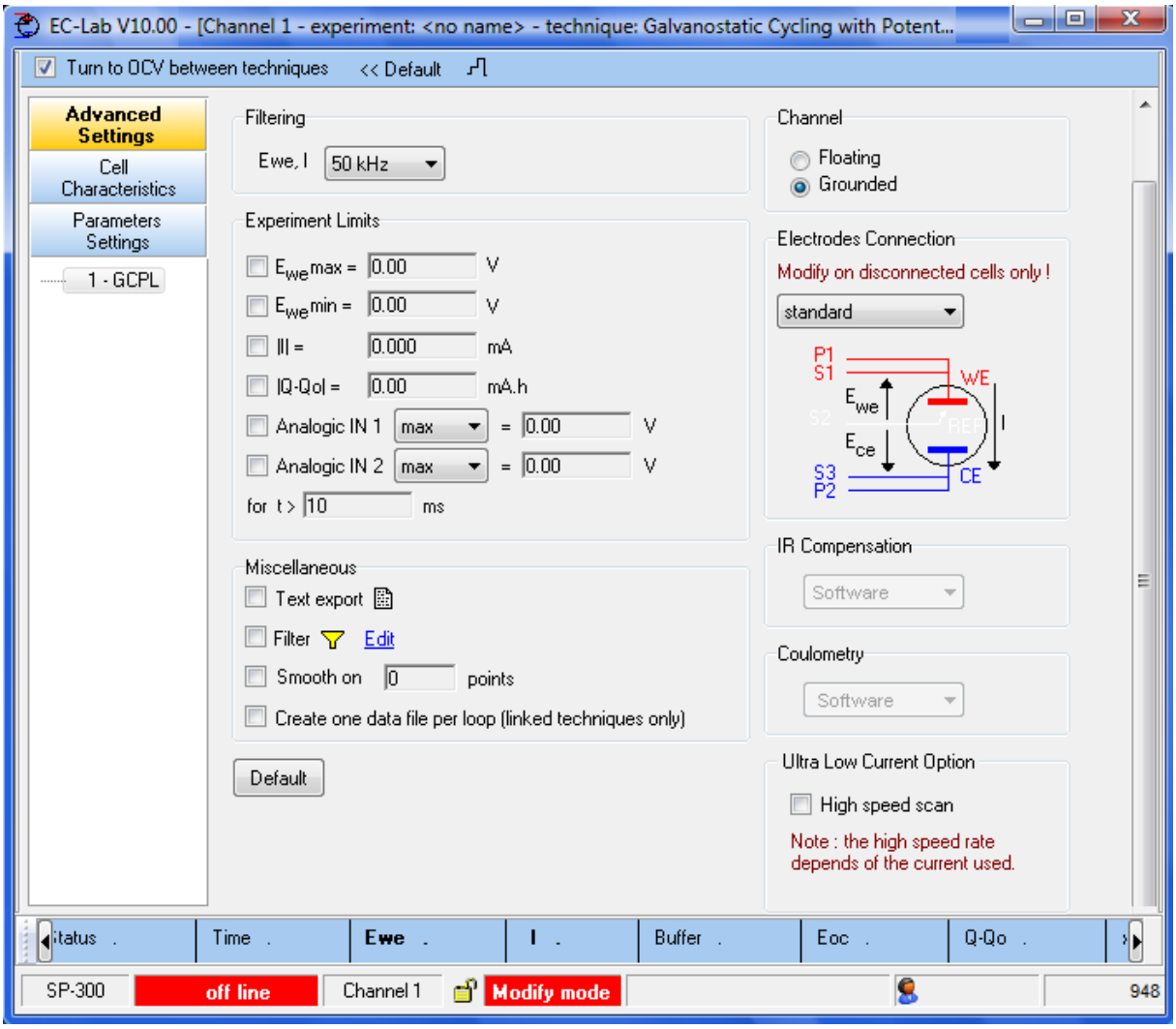


Fig. 41: Advanced settings window for SP-300 and SP-200 instruments.

Note: the “Advanced setting” window is available for all the protocols.

2.2.6.1 Compliance

The compliance corresponds to the potential range of the Counter Electrode versus the Working Electrode potential. This option has to be modified only for electrochemical cells with more than 10 V potential difference between the counter and the working electrode. One can change the instrument compliance voltage between the CE and the WE electrodes from – 20 V → 0 V to 0 V → 20 V, by steps of 1 V. In all the ranges the control and measurement of the variables are available.

The default compliance of CE vs. WE is ± 10 V. For example, while working with a 12 V battery, with the CE electrode connected to the minus and the WE connected to the plus, the potential of CE vs. WE will be – 12 V. That is not in the default compliance. In order to have the CE potential in the right compliance, set the CE vs. WE compliance from – 15 V to + 5 V.

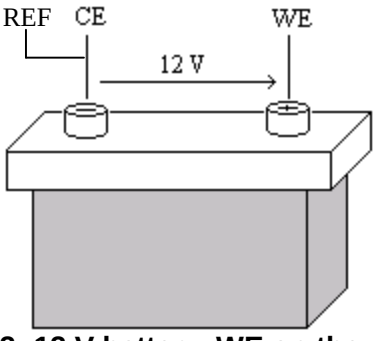


Fig. 42: 12 V battery, WE on the plus.

When the working electrode is connected to the minus and the counter electrode to the plus, the potential of CE versus WE will be + 12 V. Then the compliance must be shifted between – 5 and + 15 V.

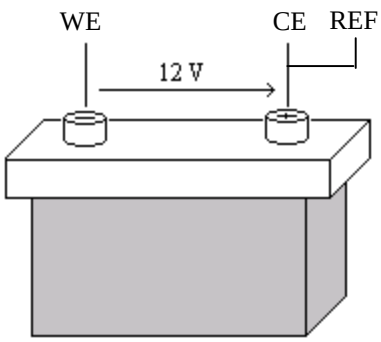


Fig. 43: 12 V battery, WE on the minus.

Warning: the compliance must be properly set before connecting the cells to avoid cell disturbance.

For SP-300 and SP-200 instruments, the compliance is not adjustable and is equal to +/- 12 V. With the 1 A/48 V booster the compliance is +/- 48 V.
For HCP-1005, HCP-803 and CLB-500, compliance value is fixed.

2.2.6.2 Electrodes connections

2.2.6.2.1 CE to Ground connection mode

It is possible to work with several WE (several RE) and one CE in the same bath. Then, counter electrodes must be connected together to the Ref1 lead and ground.

For VMP3 technology:

Disconnect the cables from the cell, select Electrodes connection = CE to ground and reconnect the cell as follows:
- CE and Ref3 leads to the working electrode
- Ref2 lead to the reference electrode
- GROUND and Ref1 leads to the counter electrode

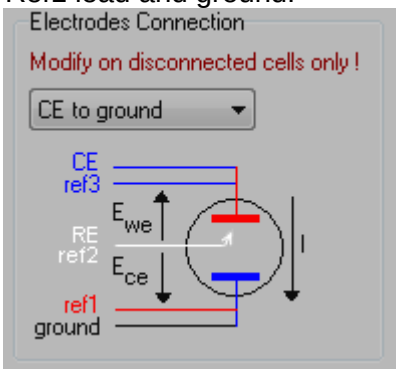


Fig. 44: Configuration CE to ground (N'Stat) for VMP3 technology.

For SP-300 technology:

Disconnect the cables from the cell, select Electrodes connection = CE to ground and reconnect the cell as follows:
- P1 and S1 leads to the working electrode
- S2 lead to the reference electrode
- GROUND and S3 leads to the counter electrode

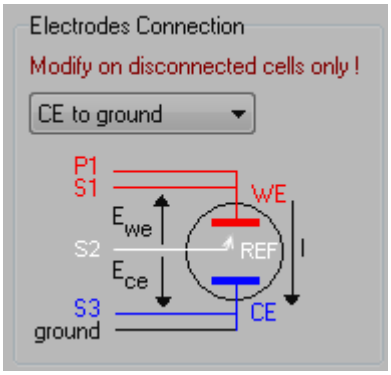


Fig. 45: Configuration CE to ground (N'Stat) for SP-300 technology.

To set the standard connection, proceed in the same way: disconnect the electrodes from the cell, select Electrodes connection = standard and set the next connections:
- Ref1 and WE leads to the working electrode for VMP3 technology or P1 and S1 leads to the working electrode for SP-300 technology
- Ref2 leads to the reference electrode for VMP3 technology or S2 leads to the reference electrode for SP-300 technology
- CE and Ref3 leads to the counter electrode for VMP3 technology or S3 and P2 leads to the counter electrode for SP-300 technology

Refer to the “Installation and configuration manual” for more details on the CE to ground connection.

Warning: it is important to disconnect the electrodes from the cell, before changing the electrode connection, because of the difference between the leads assignment, the OCV may not be properly applied.

Note: with CE to ground connection, CE vs. WE compliance is set to ± 10 V.
The CE to ground option is not available with the ZRA protocol (Zero Resistance Ammeter).

2.2.6.2.2 WE to Ground connection mode

In addition to the CE to ground mode, a “WE to ground” connection mode is available with the SP-200 and SP-300.

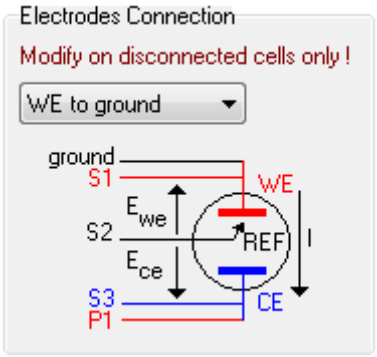


Fig. 46: WE to ground connection for SP200/300.

This configuration is very useful for hydrogen permeation measurements where one working electrode is grounded and connected with two different couple of counter electrode and reference electrode.

2.2.6.3 Experiment limits

Most of protocols already have potential, current or charge limits (for example Galvanostatic Cycling with Potential Limitation (GCPL): limit E_{we} to E_M and $|\Delta Q|$ to ΔQ_M, ...) that are used to make decision (in general, the next step) during the experiment run.

The experiment limits are of another kind. They have been designed to enter higher limits than the limits set into the protocols to protect cells against damages. Once an experiment limit is reached, the experiment is paused. Then the user can correct the settings and continue the run with the Resume button or stop the experiment.

To select an experiment limit, check the limit and enter a value and a time, for example: E_{we} max = 5 V, for t > 100 ms. Then the limit will be reached if E_{we} is greater than 5 V during 100 ms. Once selected, an experiment limit is active during the whole experiment run.

Warning: the experiment limits cannot be modified during the experiment run and must be set before.

2.2.6.4 Miscellaneaous

2.2.6.4.1 Text export

This option allows the user to export data automatically in text format during the experiment (on-line exportation). A new file is created with the same name as the raw data file but with an .mpt extension.

2.2.6.4.2 Filter

This option allows the user to filter by the mean of the software the data just after the run by ticking this box before running the experiment. A new file is created with the same name as the raw data file but with an .mpp extension. . This Filter tool is described in the paragraph dedicated to Analysis tools.

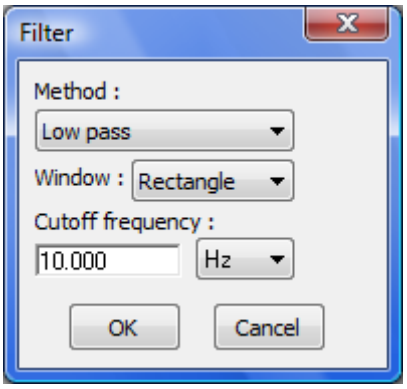


Fig. 47: Filter window.

2.2.6.4.3 Smooth with sliding average.

For all the protocols, the user can smooth all values (I, E_{we}, E_{ce}, Aux1…) with a sliding average. To proceed, check smooth and enter the smooth window size (between 2 and 100 points).

2.2.6.4.4 Create one data file per loop

This option offers the possibility to create one data file per loop for each technique of a linked experiment. Then the data files will have a prefix number to define the order in the experiment.

2.2.6.5 Filtrering

This option is only available for the SP-300 technology. It is possible to filter potential (E) and current (I) by hardware. Three filters exist 5 Hz, 1 kHz and 50 kHz. It is also possible to obtain the raw data by selecting No filter (None).

2.2.6.6 Channel

This menu is only available for the SP-300 technology. The Channel menu permits the selection between Grounded and Floating mode for the used channel.

2.2.6.7 Ultra low current option

This option is only available with the SP-300 technology and more especially when the Ultra Low Current option is connected to the channel. This option is necessary when low current ability at relatively high speed is required. In these extreme conditions, measurements may be distorted. For instance, a loop appears at the vertex (Fig. 48).

The value of current scan where the correction must be applied depends on the intrinsic characteristics of the cell (type of electrode, distance between electrodes, ...). A correction is offered in the “Advanced setting” window. This option is automatically selected when Ultra Low current option is connected.

Note that, if the Ultra Low Current option box is ticked, the data may be noisier especially for ranges below 1 nA (Fig. 49). It is possible to reduce the noise by filter the data (available in the “**Math**” menu of the “**Analysis**” menu).

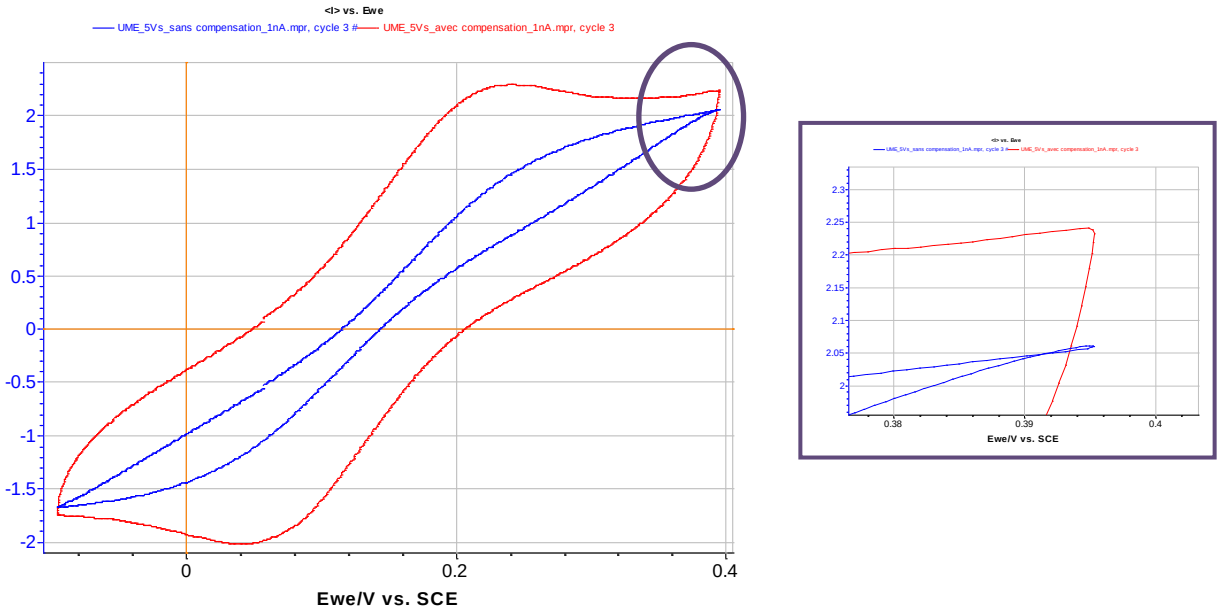


Fig. 48: CV carried out with an Ultra Microelectrode of 10 µm in a solution of ferrocene in EtOH with TBAP as supporting salt. The range of current is 1 nA and scan rate is 5 $V.s^{-1}$. Zoom at the vertex.

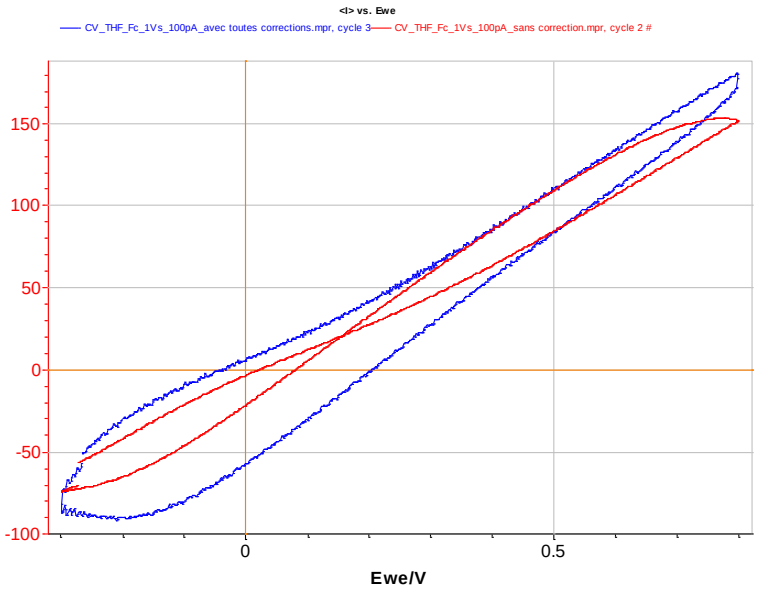


Fig. 49: CV carried out with Ultra Microelectrode of 10 µm in a solution of ferrocene in THF without any supporting salt. The range of current is 100 pA and scan rate is 1 $V.s^{-1}$.

2.2.7 Accepting and saving settings

Once you have set the parameters of your experiment, click on the **Accept** icon . It validates the parameter settings, the cell characteristics and the advanced settings and sends them to the instrument. If the option is activated in the **Config\option\Warning menu**, the following window will appear before to accepting the settings:

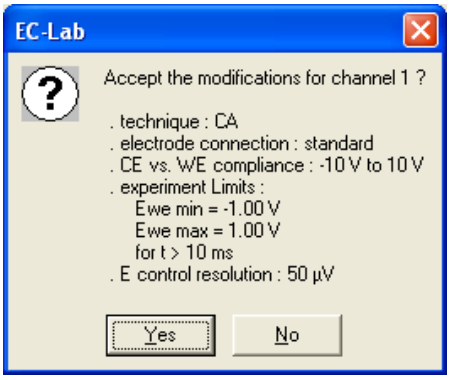

EC-Lab
Accept the modifications for channel 1 ?
. technique : CA
. electrode connection : standard
. CE vs. WE compliance : -10 V to 10 V
. experiment Limits :
Ewe min = -1.00 V
Ewe max = 1.00 V
for t > 10 ms
. E control resolution : 50 µV
Yes
No

Fig. 50: Summary window before to Accept settings.

This window summarizes several parameters of the experiment. Click on **Yes** to accept the settings and start the experiment.
The settings can be set as default settings for the current technique. Right click on the mouse and select "**Set settings as Default**". The parameter settings can be saved as an *.mps file in Experiment\save as\ or right click on **Save Experiment…**, or click on .

2.2.8 Running acquisition

Click on the **Run** button . A filename selection window will appear:

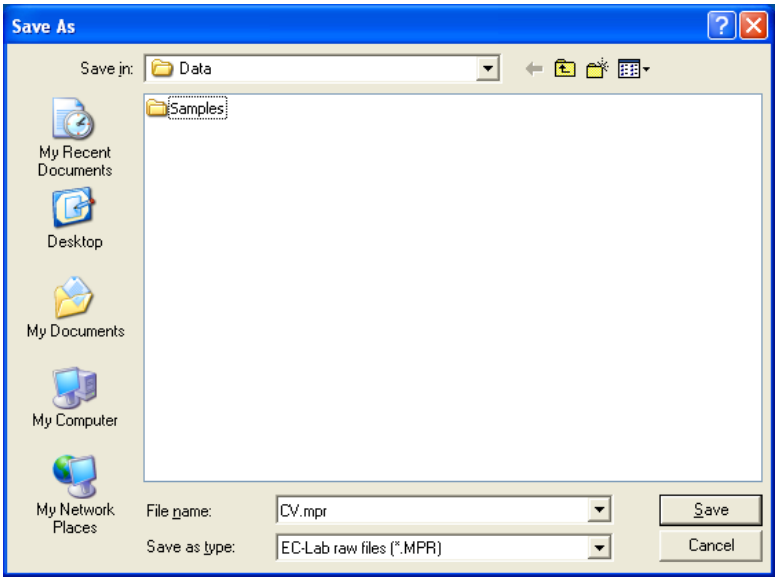


Fig. 51: Filename selection window.

The default folder to save the data is called "Data". The user can choose and create another folder to save his data files. Type the filename.

Note: the filenames can be forced to end with the channel number using the **Config, Option...** command. This option is always fixed for grouped channels.

Clicking **Save** or pressing <ENTER> will start the experiment, and the **Run** button switches to the **Stop** button.
Two files are created when running the experiment: a binary raw data file, with an **.mpr** extension automatically added, and a text file which contains all the information for the experiment (the selected protocol, initial settings, instrument IP and channel N°, files directory, etc.). This last file is called the Log of the experiment. It has the same name as the raw file but with an **.mpl** extension.

2.3 Available commands during the run

During the experiment several commands remain actives. Most of the parameters of the flow diagram can be changed while the experiment is running. Changes are saved in the log file.

2.3.1 Stop and Pause

Clicking on the **Stop** button will display a message asking for confirmation. Clicking OK, stops the measurement. At that time a binary version of the **.mpl** file is appended to the **.mpr** file. A raw data file is then obtained which contains all information on the experiment. The user can decide to clear the **.mpl** Log file (to save place), or to keep it in order to continue the "Log" of the experiment using a word processor.

Clicking on the **Pause** button will lead to a suspension in the progress of the protocol and in the measurement recordings. The cell will be disconnected from the current generator (but not from the potential measurements). Then the **Pause** button switches to the **Resume** button and clicking on this button continues the experiment (with a gap corresponding to the pause time).

2.3.2 Modifying an experiment in progress

The **Modify** button enables the user to modify most of the parameter settings while the experiment is running.

The new set of parameters is sent to the instrument when clicking on the **Accept** button . It is taken into account within 200 µs for instrumentsof the VMP3 family and SP-300 and SP-200 and 20 ms for the VMP and the MPG. All information on the change, the time it was done, the new settings etc., is appended to the Log file (see section 3.2.6, page 70). Note that a warning message could appear before accepting the modification if this option is selected in **Config\Option\Warning**. Among all the parameters, some of them cannot be modified on the fly such as Irange, Erange and Bandwidth.

2.4 Multi-channel selection: Grouped, Synchronized or stack experiments

This section is dedicated to potentiostats/galvanostats units including more than one channel in the chassis.

2.4.1 Grouped or synchronized experiments

It is possible to run the same protocol, with synchronized start on several channels (this is what we call to group channels), or to synchronize different techniques start on several channels (this is what we call to synchronize channels).
Note: in Group mode, it is possible to choose to begin the experiment with the average potentials value of all the selected channels (by ticking the box “Start grouped channels at averaged potential”) or to begin the experiment on each channel with its own potential.

Click on the **Modify** button then, in the **Edit** menu select “**Group/Synchronize channel X**” (where X is the number of the selected channel) or select this option in the right click menu. The following window appears:

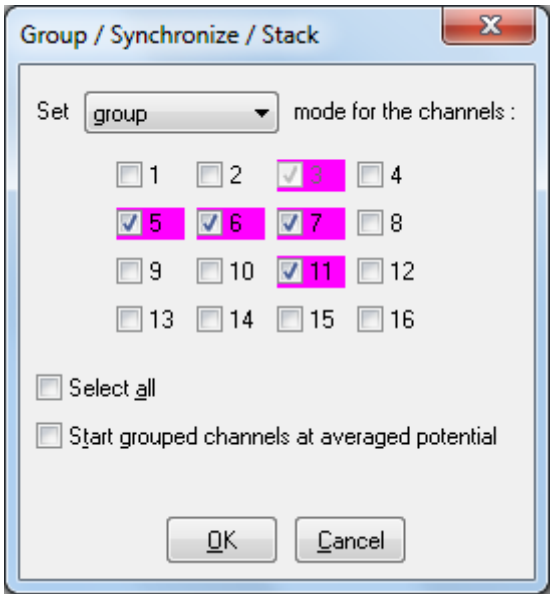


Fig. 52: Group/Synchronize/Stack window.

According to the selected channel (here channel 1 because the corresponding box is locked), the user can add other channels to either be grouped with channel 1 or be synchronized with channel 1. In this example channels 14, 15 and 16 are grouped with channel 1. For synchronized channels, the user can choose whether or not to stop channels together (at the same time). Channels belonging to the same group appear with the same colour.

One can see that other series of channels are grouped or synchronized together. To know if the other channels are grouped or synchronized, the user must show the global view in the “View” menu:

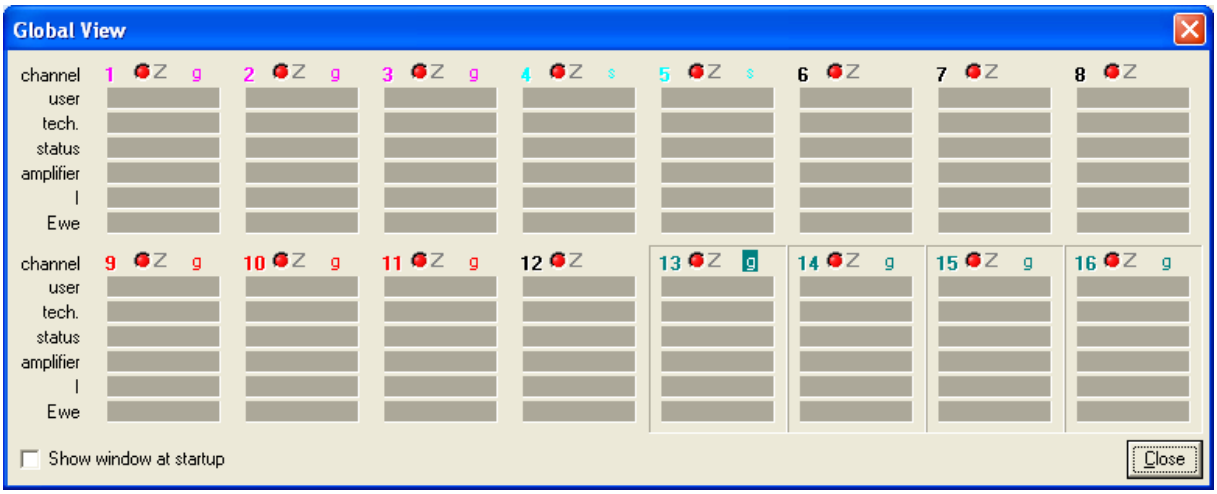


Fig. 53: Global view to show the Grouped and synchronized channels.

Grouped channels are marked with a "g" in the 16 channels global view window and synchronized channels are marked with an "s".
Now one can see that channels 1, 2, and 3 are grouped together. Channels 4 and 5 are synchronized. Channels 9, 10 and 11 are grouped and channels 13, 14, 15 and 16 are grouped.

To ungroup or unsynchronized channels, the user must select one of the required channels before opening the group/synchronize window to unselect the channels. For example for channels 1 to 3, the user must select one of these channels and then uncheck the boxes.
Note: another way to group or synchronize channel is with keyboard shortcuts:

1- To group channels, first click on the **Modify** button and then select the channels while pressing the SHIFT key.

To deselect a channel from a group, click on the **Modify** button and deselect the channel while pressing the SHIFT key.

2- To synchronize channels, proceed in the same way as for grouping, but with the CTRL key instead of the SHIFT key.

3- Channel with linked experiments can either be grouped or synchronized.

2.4.2 Stack experiments

Our multichannel units can be used for measurements on a stack of cells in series (for example batteries, fuel cells or solar cells). In this case, one channel is used as a master channel to control the whole stack and the other are managed by the master and used to do measurements on each element of the stack. In series, the current crossing each element is the same and it is the current of the full stack. But the voltage of the stack in series is the sum of the voltage of each element of the stack. The slave channels are used to measure

the voltage of each element. The master channel controls the full stack. Of course to do that a current booster or a load box must be coupled to the master channel.

When launching the EC-lab software, if a multichannel system is detected the opening window will propose to create a "**New Stack**" experiment or to "**Load a Stack Setting**".

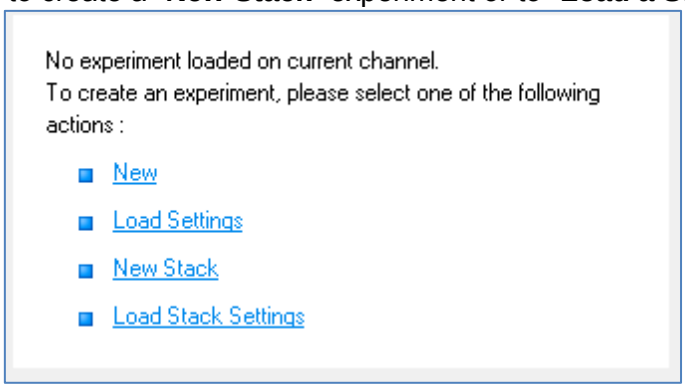

No experiment loaded on current channel.
To create an experiment, please select one of the following actions :
New
Load Settings
New Stack
Load Stack Settings

Fig. 54: Experiment selection.

When clicking on one of these choices, the following window appears for channels selection.

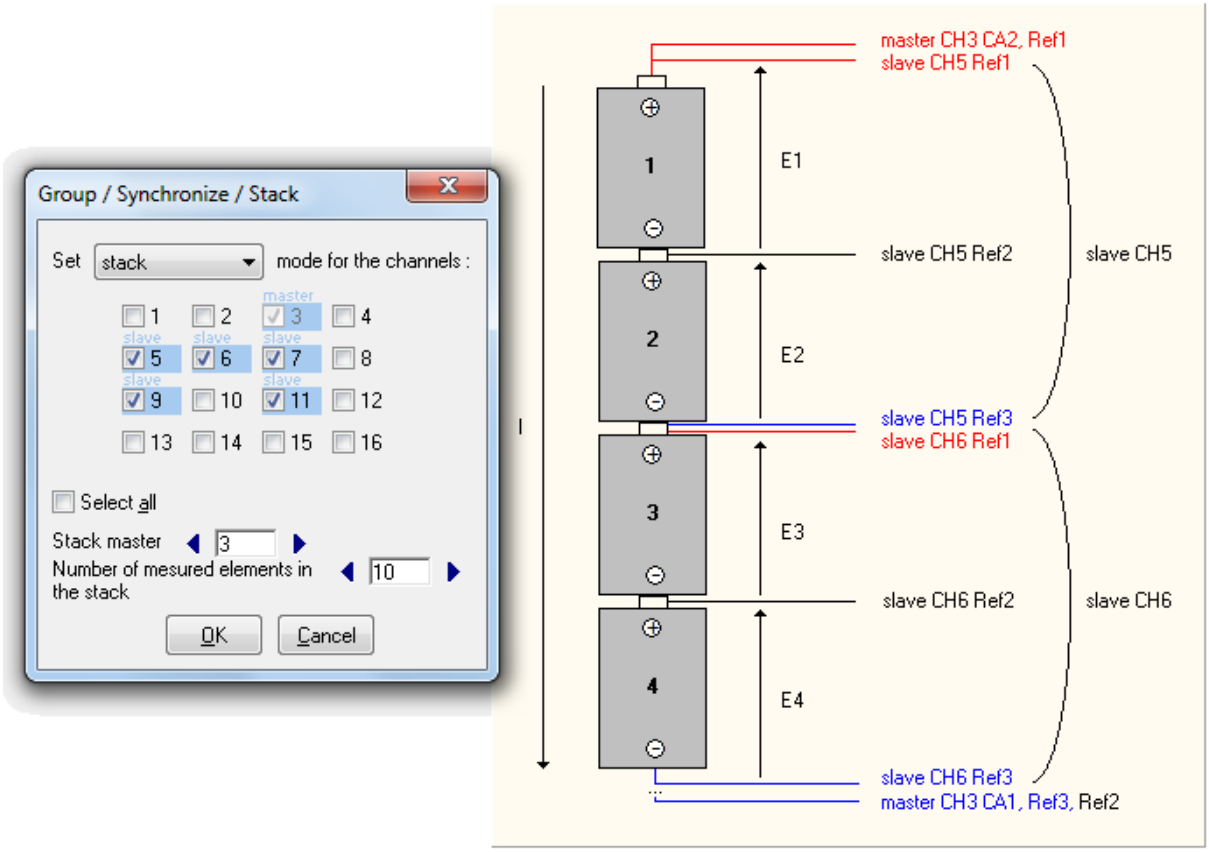


Fig. 55: Channel selection window for Stack measurements.

Thanks to the description on the right, the user will have to select the master channel and the slaves. The user must have in mind that each slave channel will measure the voltage of two elements as follow: E1= Ref1-Ref2, E2= Ref2-Ref3. As an example, with the picture above, the master channel is ch3 and the unit has 5 channels to follow the slaves so the total amount of measured elements in the stack is 10. But the stack can be constituted with more

than 10 elements. Only 10 elements will be measured in this configuration. On the slave channels the current wires (CA1 and CA2) are not used. Note also that most of the techniques and applications can be used and linked in “Stack” mode. When the user clicks on the “Ok” button, the “Techniques selection” window is automatically displayed. At this step the user can create the experiment with one or more techniques.

2.5 Batch mode

The batch offers the possibility to link a lot of experiments as a series of settings files. In this configuration, the computer is the master of the experiment sending one settings file after the other (when this previous experiment is finished). The instrument is not autonomous in this case and a Network communications failure will stop the experiment. To display the batch selection window, click on “**Batch**” in the “**Tools**” menu:

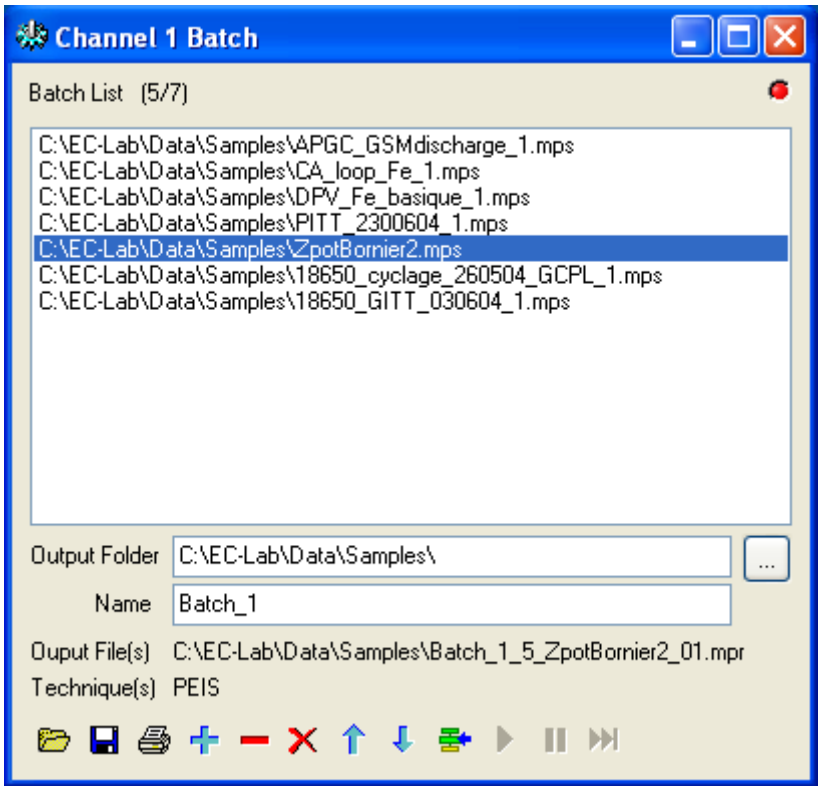


Fig. 56: Batch selection window.

When the batch window is open, it is empty. To add settings (*.mps) or data files (*.mpr) which also include the experiment settings, click on the “**+**” button then select the correct folder to find the files. Files from different folders can be loaded in the same batch.
The user must:

a. define an output folder where the created batch experiment files will be stored,
b. give a file name for the batch.

With the batch name the software will automatically generate a data file with the name for each source file:

“Batch name” + ”_” + “number in the batch list” + “_” + “source file name” + “channel number” + “.mpr”

For the user information the technique used in the selected file is displayed. Several functions are available with buttons at the bottom of the window to open, save, or print a batch, to add, remove move up and down, and insert setting files into the batch.

During the Run, the user can pause the experiment and go to the next settings file.

Note: if the number of techniques is lower than 20, it is often more convenient to use linked techniques.

2.6 Data properties

2.6.1 Type of data files

Several files using your filename with different extensions (.mp*) are created:

File extension	description
.mpr	Raw data binary file, which contains the current parameter settings (refreshed at each modification) of the detailed flow-diagram and cell characteristic windows. This file includes all the information of the .mps file.
.mps	Setting file, which contains all the parameters of the experiment. The settings can be saved as default for a given technique. It corresponds to the header of the raw data file. This file can also be generated for linked techniques.
.mpl	Text file, which contains the experiment conditions: the instrument IP number, the channel number, the username, the filename and its location, the parameter settings and the cell characteristics at the beginning of the experiment.
.mpp	Temporary binary file, available for particular protocols, derived from the .mpr file. This file is used for real time display of parameters obtained by raw data processing e.g. the integrated charge since the start of the experiment, the average current between two recordings (chronocoulometry).
.mpt	The .mpt file is a text format file generated when the user exports the raw .mpr file in text format.
.mgr	Hidden file including the graphic properties of the corresponding raw .mpr file.
.mgp	As with the mgr file, the .mgp file is hidden and includes the graphic properties of the processed file (.mpp).
.fit	This file is generated when the user makes one or several fits on an .mpr or a .mpp. The results of the fits are saved one after the other when the user clicks on the “Save” button. This file is a text file that can be opened. Each fit result can be printed alone or with other fits.

During the experiment:

- Data from measurement results are appended to the .mpr file,
- Possible modifications of the parameter settings are updated in the .mpl file and replaced in the header of the .mpr file. The .mpl file is then the "Log" of the experiment. During the experiment, this file can be read with a text editor, but users should not try to write in this file or to save it because any modification will make it unserviceable by the EC-Lab® software.

2.6.2 Variables description

Several variables are standard and common in every technique and application in the software. Every data file contains state bytes that can be hidden in the selector. Several additional variables are dependent of the technique used (cf additional variables). Depending on the techniques, some processed variables can be created (either automatically or by the

user). For EIS techniques, the variables are related to Z and admittance variables are processed.

Variable description	Variable name
Common variables	
Time (in s)	time/s
I: current (in mA)	I/mA
E_{we}: WE potential versus REF (in V)	E_{we}/V
dq : charge increment between two recorded values (in mA.h)	dq/mA.h
E_{ctrl}: potential control (in V)	control/V
I_{ctrl}: current control (in mA)	control/mA
E_{ctrl}/I_{ctrl}: potential or current control (in V or mA)	control/V/mA
E_{ce}: CE potential versus REF (in V)	E_{ce}/V
<I>, average current (calculated from I = dQ/dt), (in mA)	<I>/mA
State byte	
Mode = Intentio/Potentio/Relax, State byte (bits n°1 and 2)	mode
Oxidation/Reduction, State byte (bits n°3)	ox/red
Error bit, State byte (bit n°4)	error
Control changes, State byte (bit n°5)	control changes
Changes of N_s, State byte (bit n°6)	N_s changes
Experiment counter value has changed (bit n°8)	counter inc.
External devices: Temperature / rotating electrodes	
Temperature control (in °C)	control/°C
Temperature measure (in °C)	T/°C
Rotating electrode speed control value (in rpm)	speed/rpm
User defined recorded variable with its unit set as additional analog inputs	User/Unit

Variable description	Variable name
Additional variables	
Additional analog input 1 (in V)	Analog In1/V
Additional analog input 2 (in V)	Analaog In2/V
Additional analog input 3 (in V)	Analaog In3/V
dQ: charge on a potential step (in mA.h)	dQ/mA.h
ΔQ: charge on a cycle (in mA.h)	DQ/mA.h
I forward: in pulsed techniques current measured at the end of the pulse	I forward/A
I reverse: in pulsed techniques, current measured on the reverse part	I reverse/A
I delta: difference between I forward and I reverse	I delta/A
E step: in sweep pulsed techniques, potential step increment	E step/V

Variable description	Variable name
Processed variables	
log(|<I>/A|)	log(|<I>/A|)
Q-Q_0: charge from the beginning of the experiment (in mA.h)	(Q-Q_0)/mA.h
Q charge: Q for a charge cycle reinitialized every cycle	Qcharge/mA.h
Q discharge: Q for a discharge cycle reinitialized every cycle	Qdischarge/mA.h
x: normalized charge	x
"Ohmic" impedance (in Ω)	"R_i"/Ω
E_{we}-E_{ce}: WE versus CE potential (in mV)	E_{we}-E_{ce}/V
Cycle number	cycle number
Power: in CPW, calculated by E*I	P/W
Energy: in CPW calculated by E*I*t	Energy/W.h
R_p: polarization resistance in corrosimetry	R_p/Ω
I_{corr}: corrosion current resulting from R_p calculation	I_{corr}/A
E_{corr}: corrosion potential resulting from R_p calculation	E_{corr}/V
C^{-2}: Inverse of square capacitance for Mott-Schottky plot	C^{-2} (F^{-2})
C: Capacitance for Mott-Schottky plot	C (F)
Impedance	
Frequency (in Hz)	freq/Hz
|E_{we}|: module of E_{we} (V)	|E_{we}|/V
|I|: module of I (in A)	|I|/A
Phase of Z (in degrees)	Phase(Z)/deg
|Z|: module of Z (in Ω)	|Z|/Ω
Re(Z): real part of Z (in Ω)	Re(Z)/Ω
-Im(Z):-imaginary part of Z (in Ω)	-Im(Z)/Ω
<E_{we}>: averaged Ewe value for each frequency	<E >/V
<I>: averaged I value for each frequency	<I>/A
I Range: current range	I Range
Processed Impedance variables	
|Y|: Admittance magnitude (in Ω^{-1})	|Y|/Ω^{-1}
Admittance phase (in degrees)	Phase(Y)/deg
Re(Y): real part of Y (in Ω^{-1})	Re(Y)/Ω^{-1}
-Im(Y):-imaginary part of Y (in Ω^{-1})	-Im(Y)/Ω^{-1}

2.6.3 Data recording

In all the technique sequences, the user is able to define different modes for data recording. The main mode corresponds to fix the recording resolution of the measured variable (potential, current, charge,...) with at least a recording every predetermined time interval dt (from 0.1 to 9999 s). This last condition gives a minimum of recorded points in case the variation of the observed variable is less than the chosen resolution for a long period of time (potential close to equilibrium, process leading to a potential plateau, etc...).

For open circuit period (OCV) nothing is controlled and only the potential is recorded. The recording conditions for OCV periods are in time variation (dt) and/or in potential variation (dE).

For techniques with potential control, two different recording conditions are now available:

1- on a time variation and/or an instantaneous current variation (dI) and/or charge variation (dQ),
2- on an averaged current value either on a potential step (potentiodynamic mode) or a time variation (potentiostatic mode).

For techniques with current control, the recording conditions are on a time variation (dt), potential variation (dE) and/or charge variation (dQ). Recording conditions are described in the application section for each technique

If the user wants to force a periodic recording in time, he must set a large value in the recording resolution of the variable or, more simply, set the recording resolution to 0. So the box for which the resolution is 0 stays colored. This color code means that this box is not activated and also not taken into account for recording.

2.6.4 Data Saving

Each channel has its own memory buffer (small) to store data points. The recorded points of all the channels are stored in the motherboard buffer. The instrument buffer can store a number of points depending on the protocol and the number of channels working in the instrument. The buffer size increases when the number of channels in the instrument decreases.
The minimum number of points considering 1 channel is 48000 points for the VM42 module and 480000 points for the VM62 module and considering 16 channels (VMP2, VMP, MPG) is 3000 points for the VM42 module and 30000 points for the VM62 module. For the new instruments (VSP, VMP3, HCP-803, VSP, SP-150, CLB-500, HCP-1005, SP-300 and SP-200) with the new ARM communication board (delivered from 11/2005 with USB port and Ethernet port) the memory size has been extended to 640000 points for a 1-channel unit and to 40000 points considering a 16-channel configuration.
Data transfer between the instrument and the PC via the Ethernet line is automatically started when its buffer is 5 % full. Please note that the user can define the data saving frequency in the "**Option/General**" menu (see section 2.9.1, page 47). In the same menu the user can also define an automatic creation of the data file name.

2.7 Changing the channel owner

Click on **Config, User** and enter your username in the following window:

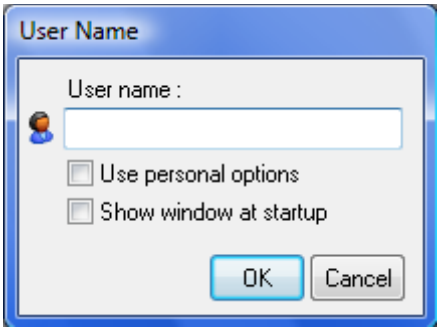


Fig. 57: User name window.

In the case where the new user will replace the current user of a channel (e.g. MyName), EC-Lab® software displays a warning message: "**WARNING: channel x belongs to "MyName". By accepting the modification you will replace the current owner. Do you want to continue?**"
It is not possible to change the user name of a channel when an experiment is running. Changing a channel owner is only possible when the channel is stopped.

2.8 Virtual potentiostat

When the software is not connected to the instrument it is possible to prepare a setup of parameters in the virtual mode including boosters and options for the instrument. When the instrument is selected the corresponding number of available channels is displayed with additional choice for amplifiers and cables (for SP-200/300 if required). In this mode the user can create a setup and save it as a *.mps file.

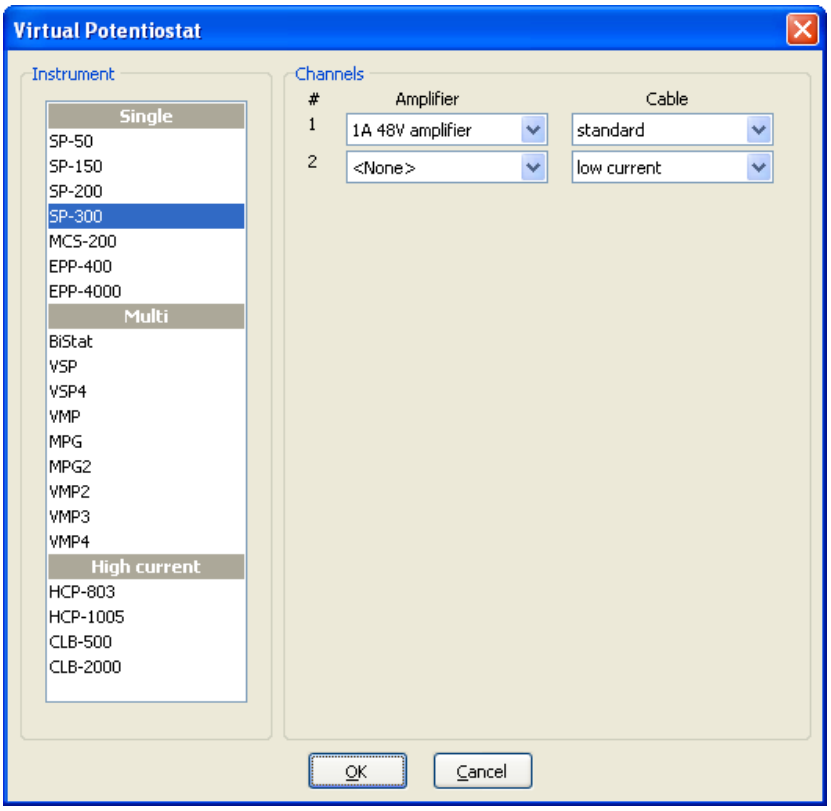


Fig. 58: SP-300 Virtual mode.

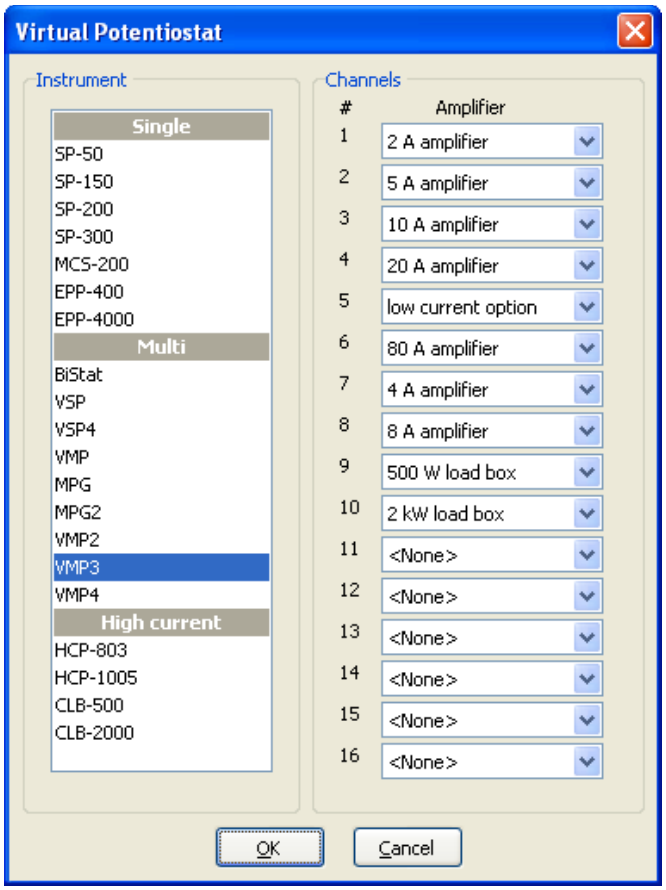


Fig. 59: VMP3 Virtual mode.

2.9 Configuration options

Choose the **Config, Options...** menu to load the Option window:

2.9.1 General options

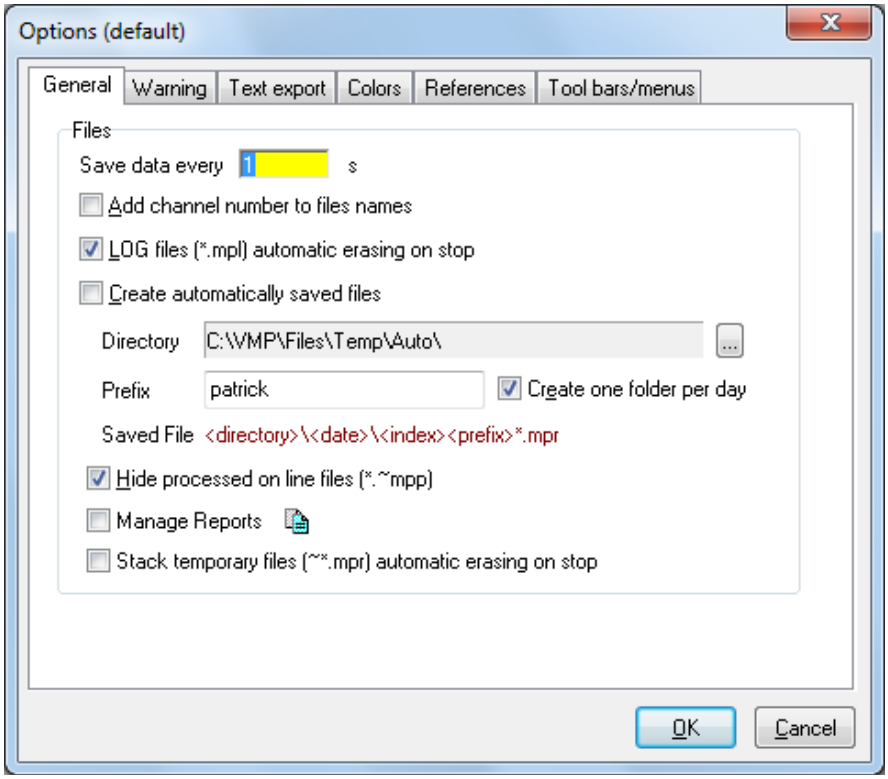


Fig. 60: Option window, General tab.

The general options window is made with two frames. The first one is for the files, and the second one is for the Graph. In the files frame several options are offered to the user:

- **"Save data every…s"** defines the data transfer rate. Enter a non-zero time value into the edit box. The data will be then transferred at this defined time interval.
- Select the automatic adding of the channel number to filenames.
- Erase the Log file automatically on stop.
- Create an automatic data saving. The user has to choose the directory to save the data file. He must define the prefix name and the software will automatically add the date and the index number.
- By default the on-line automatically processed files are hidden to reduce the number of files in directories. The on-line processed variables are now automatically displayed on the graphic window.
- Ability to manage reports of the experiment.

In the **Graph Optimization** frame:

- **Draw only lines over 1000 points** can be used in experiments with big data files. This display mode shows only the lines on the curve and hide markers for a fast display.
- **Undersample traces over 1000 points** accelerate the graphic display of large data files with the following undersampling:

- no undersampling for data files less than 10 000 points
- 1 point on 2 for data files from 10 000 to 20 000 points
- 1 point on 3 for data files from 20 000 to 30 000 points
- etc…

2.9.2 Warning options

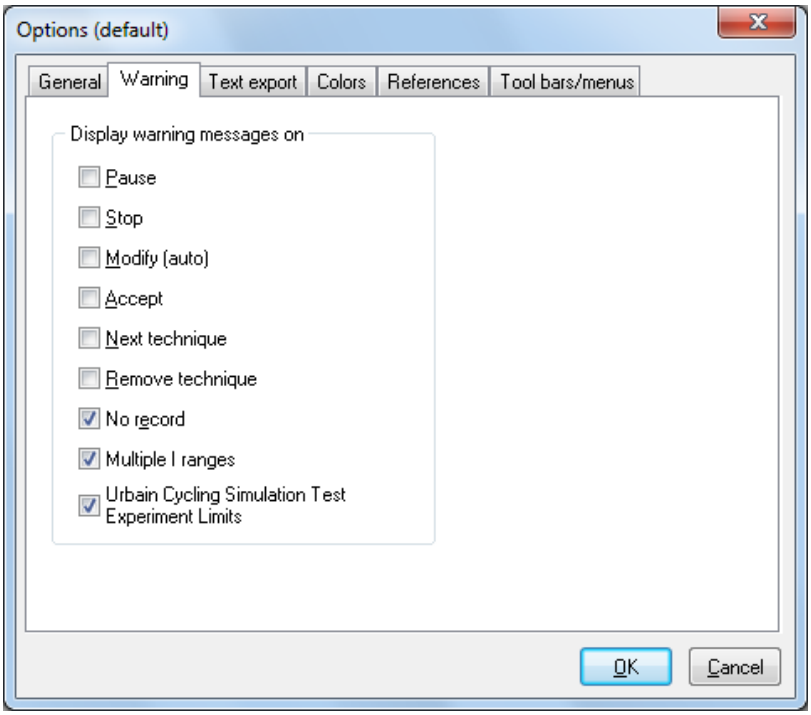


Fig. 61: Option window, Warning tab.

- Display or hide warning messages when the following functions are used: **Pause**, **Stop, Modify, Accept, Next technique, Remove technique, No data points recorded and Multiple I ranges** (different current ranges are selected in the different sequences).

2.9.3 Text Export options

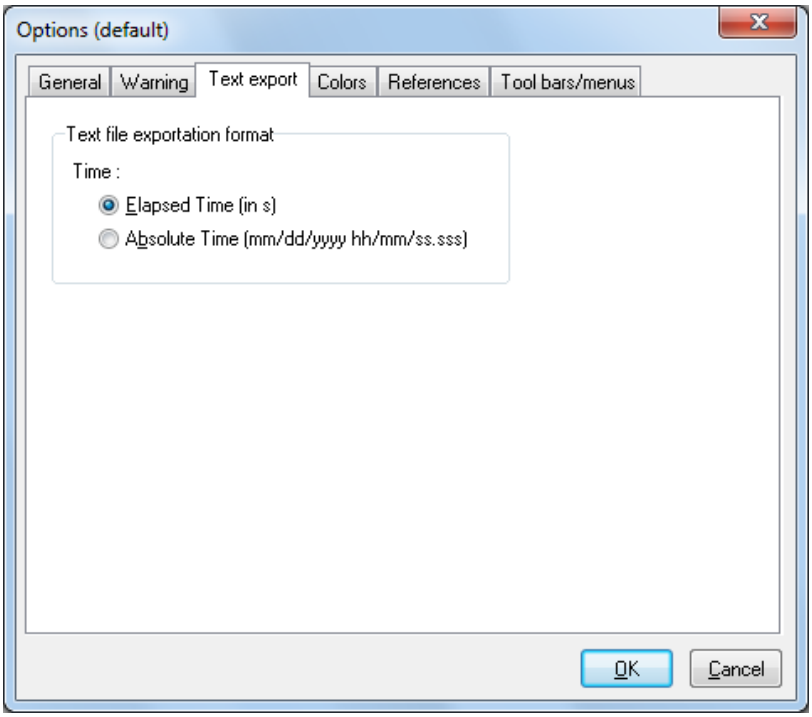


Fig. 62: Option window, Text export tab.

- Select the time recording format for the exported files.
- Export VMP2 impedance files to ZSimpWin format.

2.9.4 Color options

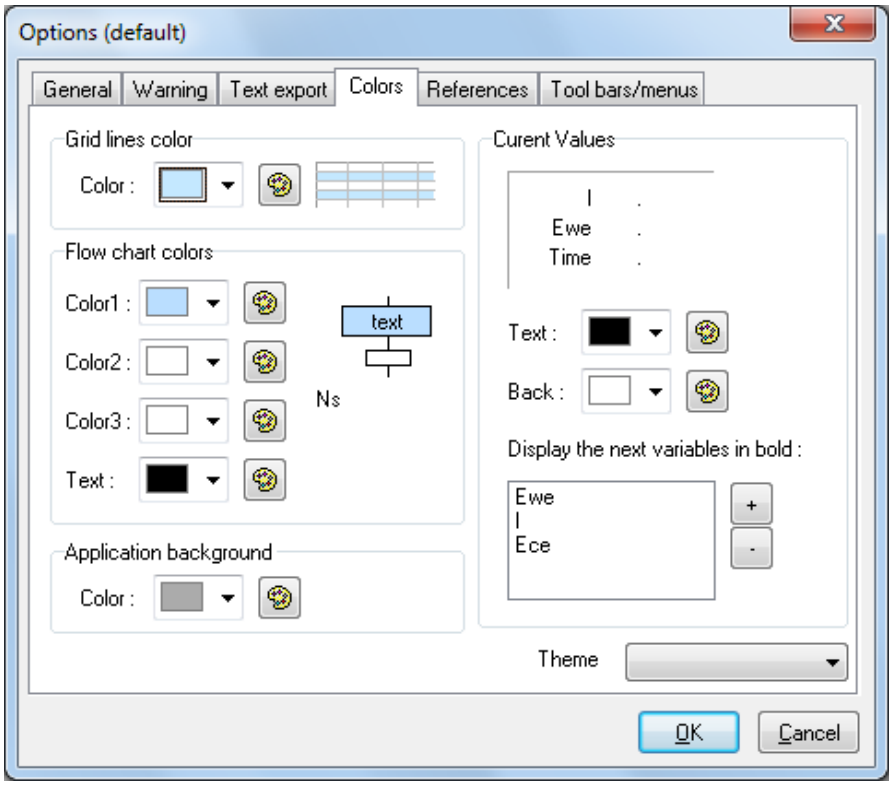


Fig. 63: Option window, Colors tab.

- Select the grid line colors, for the multi-line parameters settings (see the GCPL protocol).
- Select the flow chart's backgrounds and text colors.

The custom buttons allow the user to define additional colors that appear at the end of each list.

2.9.5 Reference electrode options

- Display all the reference electrodes registered in EC-Lab®. The default reference electrodes are in black.

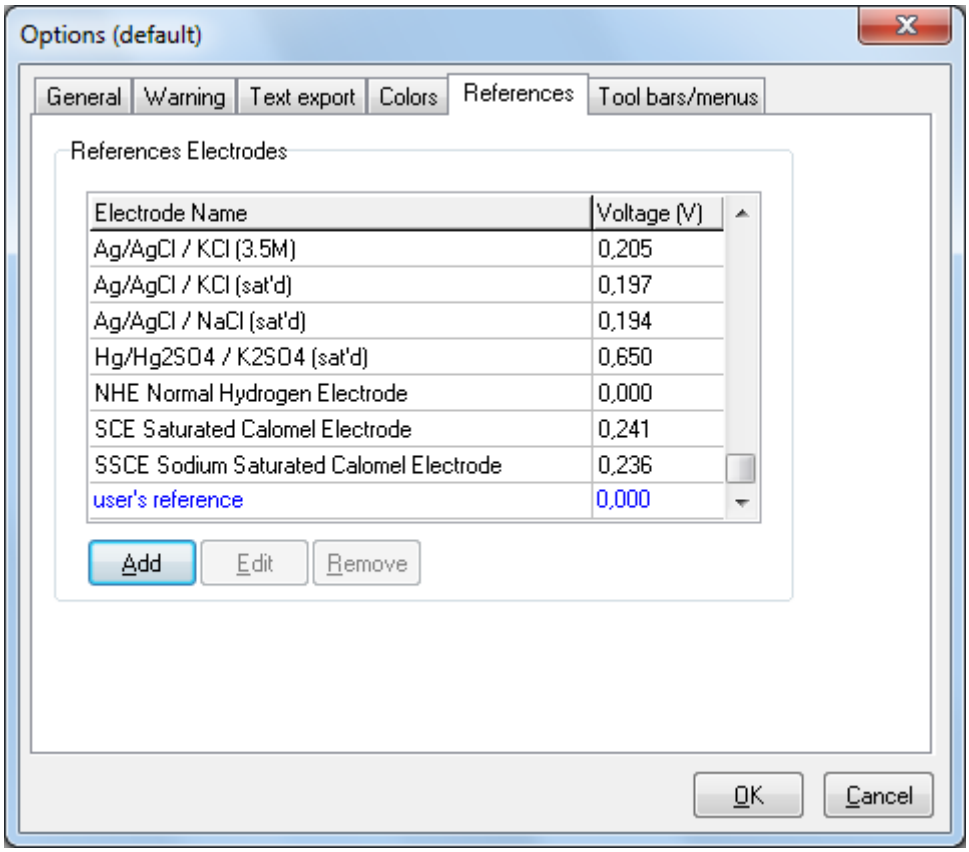
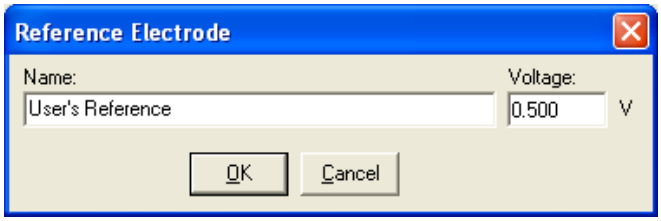


Fig. 64: Option window, references tab.

- Allows the user to add, edit, or remove his own reference electrode (and its potential vs. NHE). Then the following window appears:



The new reference electrode will now be displayed in blue characters in the table.

The standard potentials of reference electrodes have been extracted from the following references.

- Electrochemical Methods, A. J. Bard & L. R. Faulkner, Wiley, New York, 1980.
- Electrochemistry for Chemists, D. T. Sawyer, A. Sobkowiak, J. L. Roberts Jr, 2nd Ed, Wiley, New York, 1995.
- Handbook of Analytical Chemistry, L. Meites, Ed McGraw Hill, New York, 1963.

2.9.6 Tool bars options

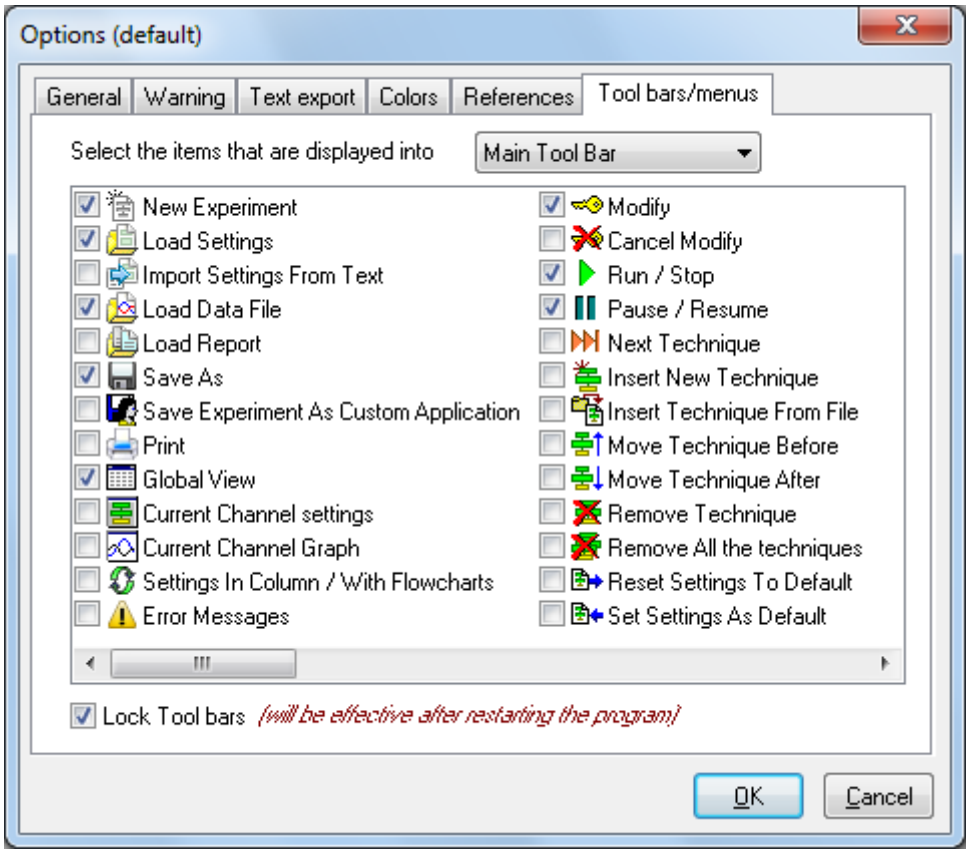


Fig. 65: Option window, Tool bars tab.

The tool bar option is made for the user's convenience. He can select icons he wants in the main tool bar and the graph tool bar from all icons available in EC-Lab® software. Both tool bars can be locked to the place chosen by the user. But this is effective only when the software is restarted. It is also possible to select the functions available on the graphic right click menu and on the settings window right click menu.

3. EC-Lab® software: Graphic Display

3.1 The Graphic window

The EC-Lab® application includes a graphic facility to display experiments on-line or/and off-line. Several independent graphic windows can be opened while an experiment is running. The user can now perform an electrochemical experiment and follow the plot on the current graphic window and fit or analyze curves resulting from previous experiments on another graphic window. The user has also the possibility to add graphs to existing graphic window. In that case the window is divided in two or more graphs (depending on the number of graphs).

When an experiment is run, the graphic window is automatically opened with selection of the corresponding result file(s). Default graphic parameters have been chosen (for example plot I vs. E for the CV technique). The user can replace the default graphic parameters by his parameters. To do so, right click on the graph, select "**Graph properties**…" and activate the box "**Save as default**".

In the case of linked techniques, two different graphic windows will be displayed, one for all voltamperometric techniques (plot versus time) and one for the impedance spectroscopy (plot versus frequency). For synchronous multi-channel protocol, all the corresponding files are displayed in the same way as linked techniques.

3.1.1 The graphic window right click menu

The graphic window contains a right click menu different from the Parameter setting window right click.

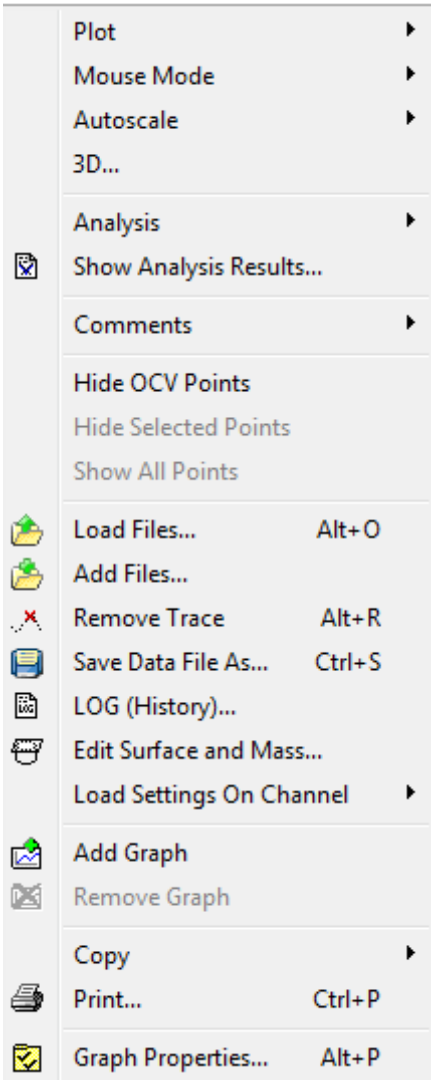


Fig. 66: Mouse right click on the graphic window.

On this right click, several frames are separated. In the first block, four menus are available:

- Plot for the selection of variables displayed on the graph, .
- Mouse Mode for the selection of graphic tools, .
- Autoscale for resize one axis or all axes, .
- 3D for displaying the graph with a 3D mode. .

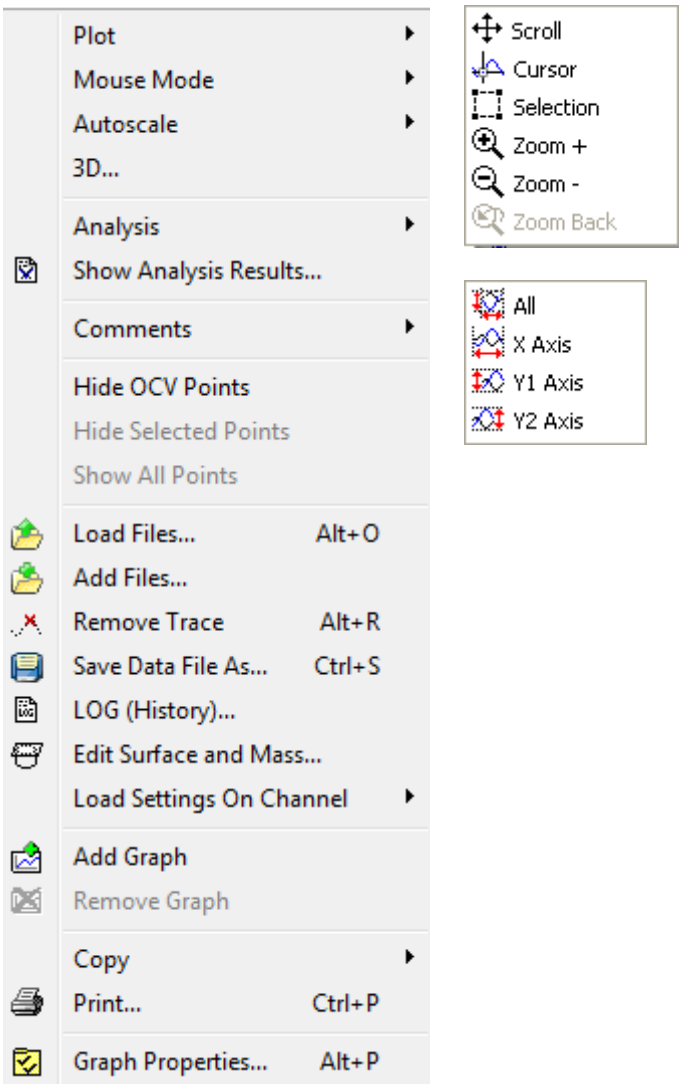


Fig. 67: Plot, Mouse mode selection and mouse auto scale options.

The Mouse mode selection contains:

- The **scroll** is used to move the curve on the graphic window.
- The **cursor** allows the user to display the coordinates of all the points of the curve.
- The **selection** allows the user to select zone of the curve (data points) either before a fit or an analysis or to hide bad data points.
- **Zoom +** and **Zoom –** are used either with a zone selection (smoothing) or by a mouse left click on the part of the curve that you want to zoom.
- **Zoom Back** is very useful when you have zoomed an undesired zone. It is not limited in the number of actions.

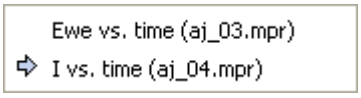
The Mouse Autoscale is made of different autoscaling functions according to each axis.

The second frame contains Analysis tools and allows displaying analysis results.
In this menu, determination of Minimum and Maximum on a curve, Linear Fit, Circle Fit and also Integral tools are available. This menu allows also the user to do a Peak and Wave analysis, but also corrosion fits (Rp Fit, Tafel Fit, CASP Fit, VASP Fit) and also Impedance analysis and simulation (ZSim, ZFit and Mott-Schottky).
These tools will be described in the Analysis part (see section 3.3 page 80).

The third frame is dedicated to comments addition on the graph with the possibility to Add and delete a comment zone and paste a comment from the clipboard.

The fourth frame is to show or hide OCV points and abnormal (artefact) data points that the user wants to remove before an analysis or a print.

The Fifth frame is more dedicated to file selection with **Load files…**, **Add files…**, **Selector…**, **LOG (history)….** The selector will be described in a following section.
The sixth frame is about the graphic display with the **Active trace…**, **Add graph** and **Remove graph**.



This option shows the active trace that can switch to the one of the other trace with a click.

The frame "**Copy** and **Print…**" includes interesting tools:

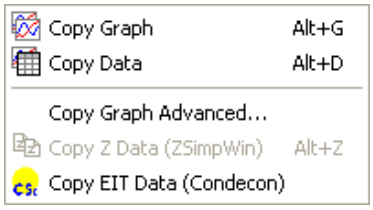


Fig. 68: Mouse copy mode.

The copy mode contains the graph copy, the data copy and the Z data copy.

- **Copy graph** is a copy of the graph to the clipboard in a bitmap format.
- **Copy data** makes a copy of the active data plot (X, Y1, Y2 displayed variables).
- **Copy Z data** copy data in ZsimpWin compatible format in order to paste data directly in this software.

The **Graph properties…** frame offers every graphic parameter.

3.1.2 Loading a data file

The EC-Lab® software is provided with sample data files. The user can load data file in **Experiment\Load Data File…** or in the graphic window with the mouse right click select **Load Files….** The following window is displayed:

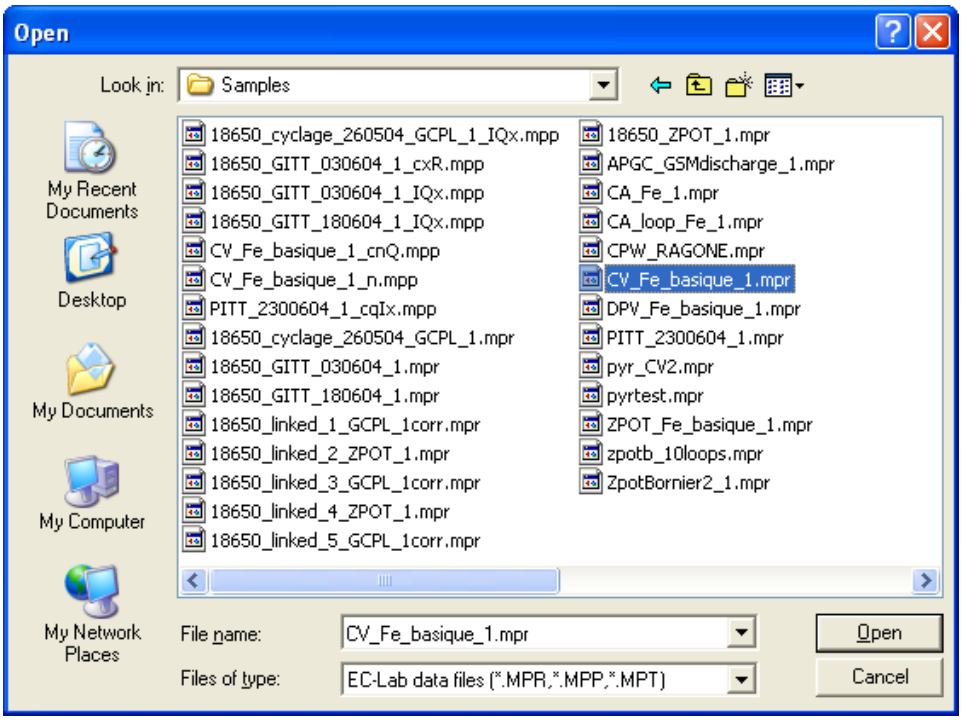


Fig. 69: Open file window.

Select the data file you want to open and click on **Open**. The user can also select and a open data file from ther manufacturers. In the file type box many file formats have been defined to help the user load data files for analysis. Most of them are text files that can be exported from software controlling other systems. The different available formats are displayed on the figure below:

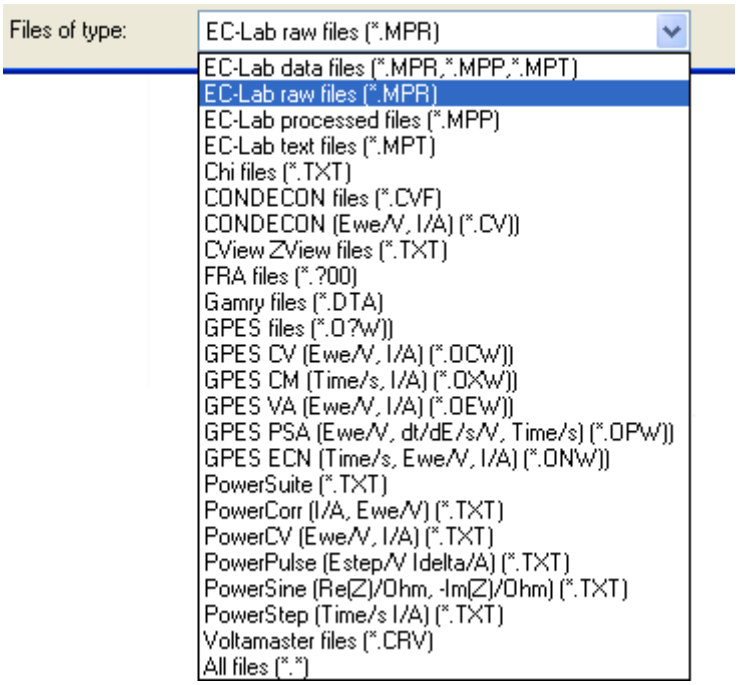


Fig. 70: File type selection.

If a file format is not listed above, the user can use the import from text option in the experiment menu to manually load its data file. This option is described in a following section.

3.1.3 EC-Lab® graphic display

Running a Cyclic Voltammetry settings will display the following graphic window. The default plot mode for the Cyclic voltammetry technique is **<I> vs. Ewe.** During the run the current recorded data point is displayed in another color and moves along the curve. This option avoids not seeing the state and the evolution of the experiment especially the position in the potential sweep when several cycles are recorded and overlaid.

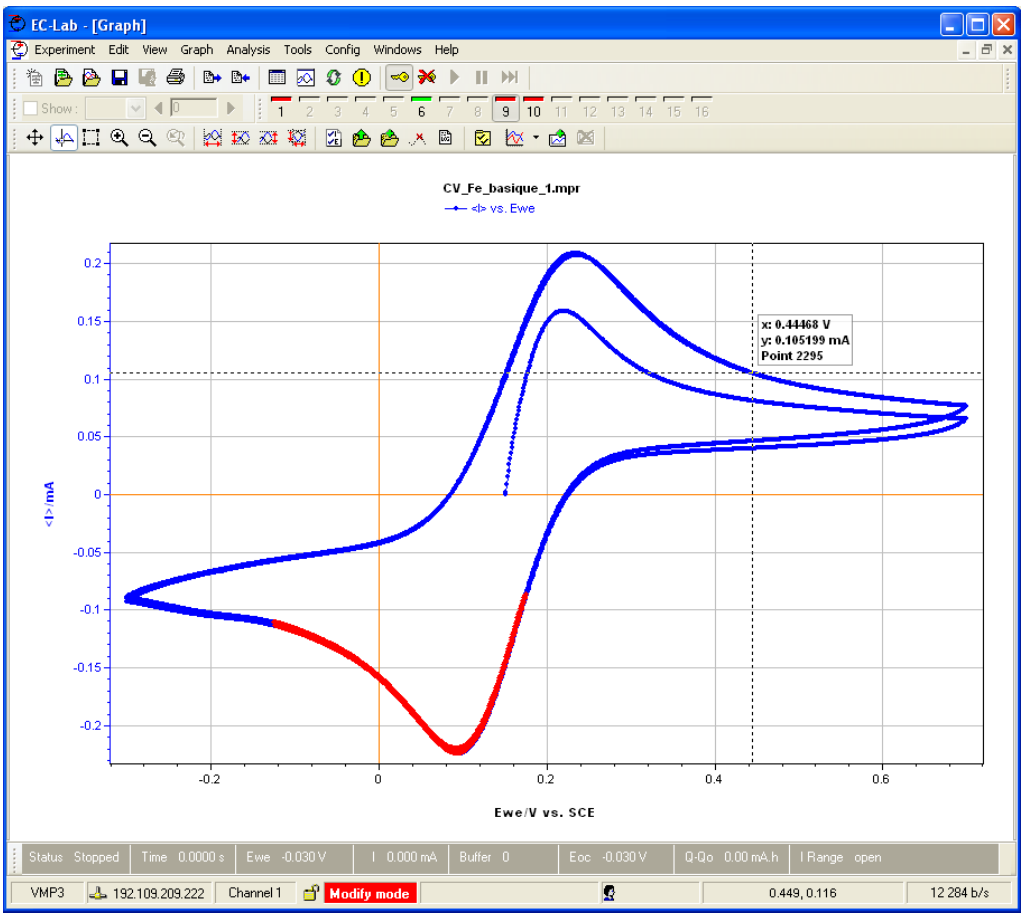


Fig. 71: Graphic window.

As can be seen, the above window (Fig. 71) displays a loaded Cyclic Voltammetry *.mpr file. On the trace a part of the curve is selected and displayed in red color. To select points, use the selection button . Select a zone by holding the left mouse button. The cursor will draw a rectangle zone around the selected points. Then release the mouse button. The selected points will be highlighted in bold red. The selected zone can be analyzed with fits or hidden from the graph before copying or fitting the graph.

The user can have every point coordinate with the mouse when holding the **SHIFT** key of the keyboard or clicking in the box. This comment box contains the point number in the experiment and the point coordinates.

Origin axes can be displayed with another color on the graphic window.

Note: On the button menu, two buttons have been added to switch easily from the current graphic window to the current setting window .

3.1.4 Graphic tool bars

When the graphic window is displayed the graphic tools bar automatically appears at the bottom. This bar is hidden on the parameter settings window.

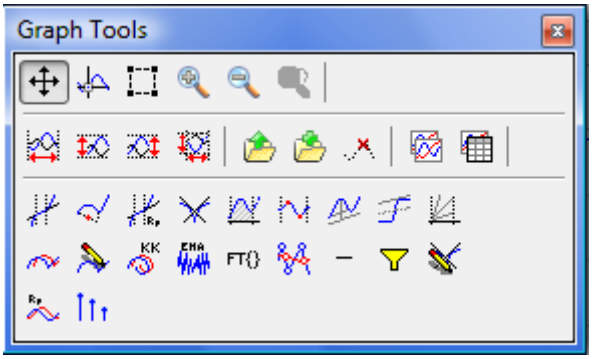


Fig. 72: Graphic tool bar.

This tool bar can contain all commands usable on the graphic window. The five first buttons are for the different mouse modes. The four buttons in the second frame concern rescaling. Data transfer from the instrument to the PC leads to immediate display in an automatic scaling mode. The graphic window is always rescaled. These buttons allow rescaling on X axis, Y1 axis, Y2 axis and every axes at the same time. Analysis tools are available, such as the linear fit, the circular fit, the R_p fit, the Tafel fit, the integral calculation, the Min/Max determination, the peak analysis, the wave analysis (dynamic regime), the linear interpolation, the filter, the ZFit, the Mott-Schottky fit. The buttons available on this bar can be configured. Several buttons can be added to the bar in the menu "**config\options\tool bars"**.

Another tool bar is available with EC-Lab® graphic window. On the left a scroll menu allows for quick plot selection among several defined representations. The available plots are dynamic and depend on the file type (time evolution or frequency evolution).

Fig. 73: rapid selection plot tool bar.

At the end of this menu, the user can find a "Custom" option that opens the File selection window for further graphic visualization. On the right part of the tool bar a "Show" option makes possible to the user to show only one cycle or one loop.
The user can define his own fast graphic displaying mode. To do that, see the section below.

3.1.5 The data file and plot selection window

Right click on the mouse and select "**Selector…**", select "**Selector…**" in EC-Lab® **Graph** menu or click on the "Selector" button to open the selection window. The following window will be displayed:

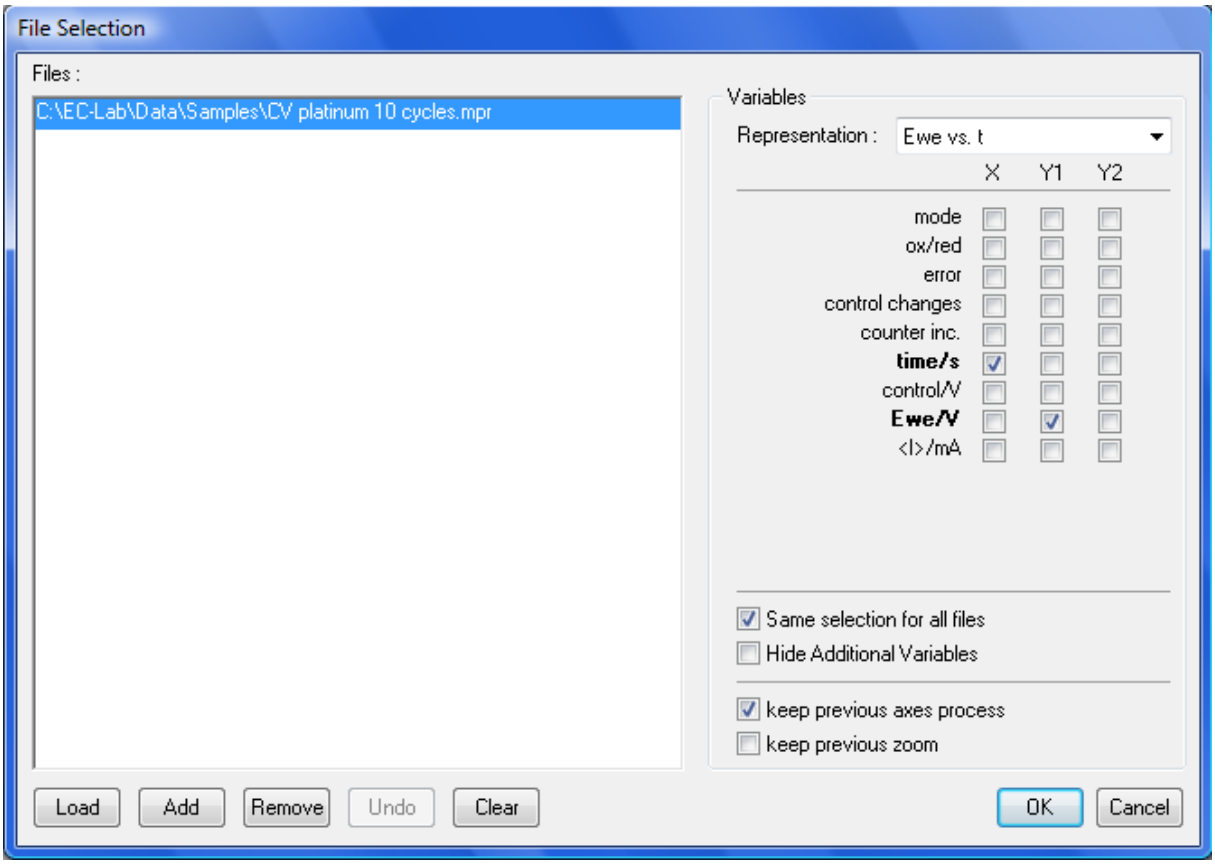


Fig. 74: File selection window.

The user can choose to plot another visualization (for example: time/s for X, E_{we}/V for Y1 and <I>/µA for Y2). The loaded file contains the recording of the following variables: the time (time/s), the working electrode controlled potential (control/V), the working electrode measured potential (E_{we}/V), the average current (average values on every potential steps, <I>/mA), and the state byte. Other variables (such as cycle number) may be displayed depending on the protocol of the experiment. The state byte includes the variables: mode, ox/red, error, control changes and counter inc. (cycle increment) that indicates different statuses of the experiment. Most of the time, the user may not be interested in showing the state byte (that is more dedicated to internal files processing). So the option **Hide Additional Variables** is checked by default. Unchecking the option will add the state byte variables to the file selection window. It is also possible to keep some previous processes or zooms by ticking the boxes **Keep previous axes process** and K**eep previous zoom**.

Several commands are available to use files:

- **Load**: replace all files by others.
- **Add**: add file(s) to the list in order to overlay curves.
- **Remove**: remove the selected file from the list.
- **Undo**: undo the last operation done.
- **Clear**: remove all files from the window.

X, Y1, and Y2 represent the X axis and two different Y axes (left and right). EC-Lab® users are able to plot data in X, Y1 coordinates or in X, Y1&Y2 coordinates. Select the variables to be displayed on a given axis by clicking the corresponding box (click again to deselect). Select **Same selection for all files** to get the same axis display for several files. A shortcut scroll menu allows a quick selection of the graph plot.

3.2 Graphic facilities

3.2.1 Cycles/Loops visualization

Since version 9.20 of the software, the cycles in the CV, CVA and SV techniques are automatically generated with no action by the user. But for experiments made with an older version the user will have to process the cycle number according to the procedure described below to display each cycle separately.
If the selected file contains linked experiments loops or several cycles then one can display specific loops or cycles. To access the cycle/Loop selection, the user has to add the cycle/loop number to the data file.
In EC-Lab® **Analysis** menu select **General Electrochemitry/Process data**. After loading the data file, select "**Cycle Number**" and "**Process"**. The following window appears:

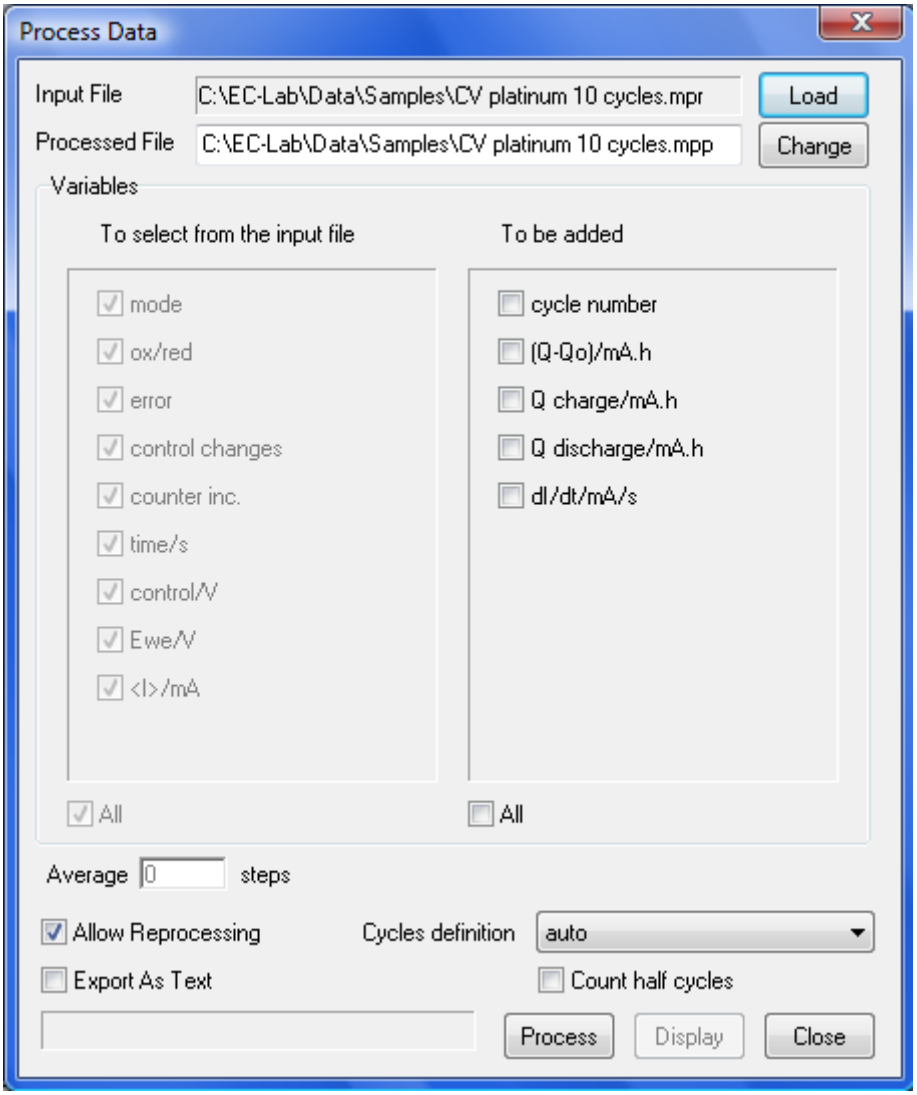


Fig. 75: Loops/cycles process.

At the end of this operation, DONE is displayed and a processed file (*.mpp) is generated in the same folder as the raw data file (*.mpr).
Click on the "**Display**" button to automatically display the processed file. A cycle selection tool is now activated on the graphic tool bar to select the cycle to display:

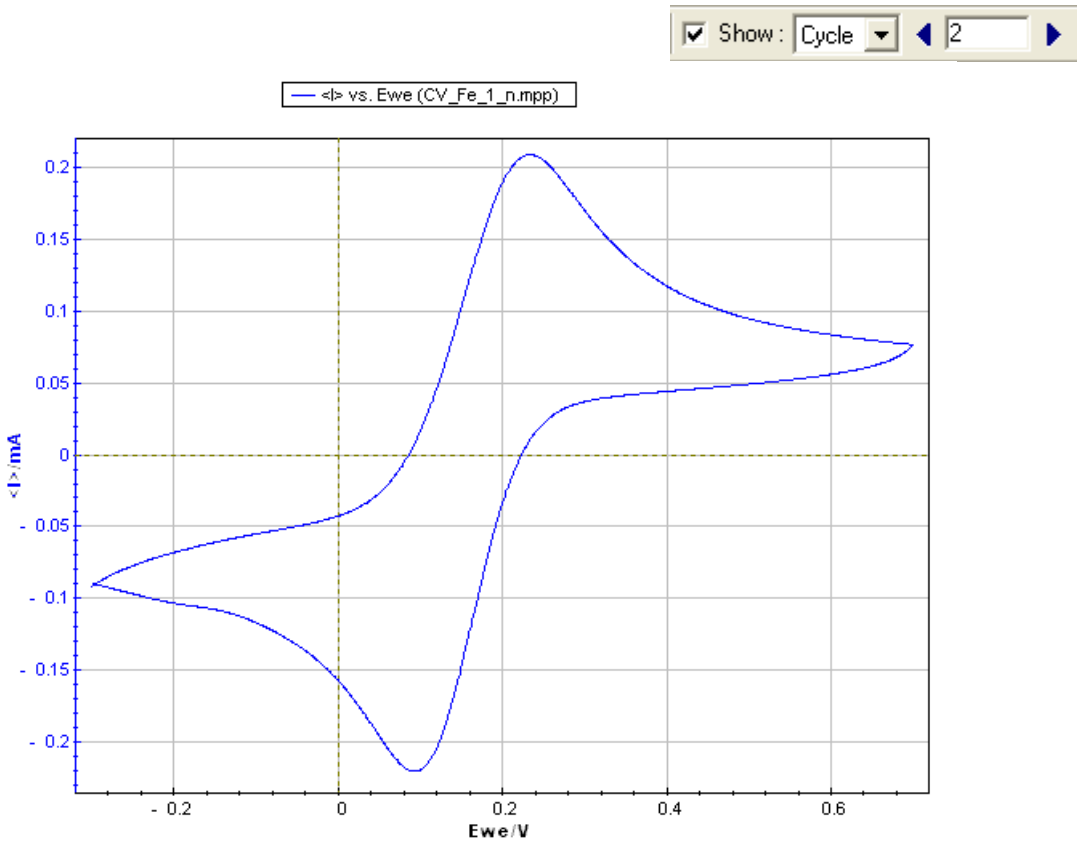


Fig. 76: Cycle selection on a processed file.

The user can see either all cycles or a selected cycle chosen with the scroll box. This option is very useful for peak analysis on a given cycle, especially in analytical electrochemistry.

Note: - If the user wants to copy data (mouse right click) and paste in a spreadsheet software only data corresponding to the displayed cycle will be copied.

- A title can be added to the data file and appear at the top of the graphic window. Right click, Select **Graph properties** and choose the **Title** tab.

3.2.2 Show/Hide points

The EC-Lab® software is equipped with a show/hide option on the right click menu. Aberrant points can now be hidden on the graph in order to perform data fitting without any troubling points. The hidden data points are not removed from the data file. They are only graphically hidden for better fitting. The data points must be selected with the selection mouse mode before being hidden. Then click on **Hide selected points** to reject points.

3.2.3 Add comments on the graph

The graphic package allows the user to add comment zones on the graph. The number of comments zones that can be added on the graph is unlimited.

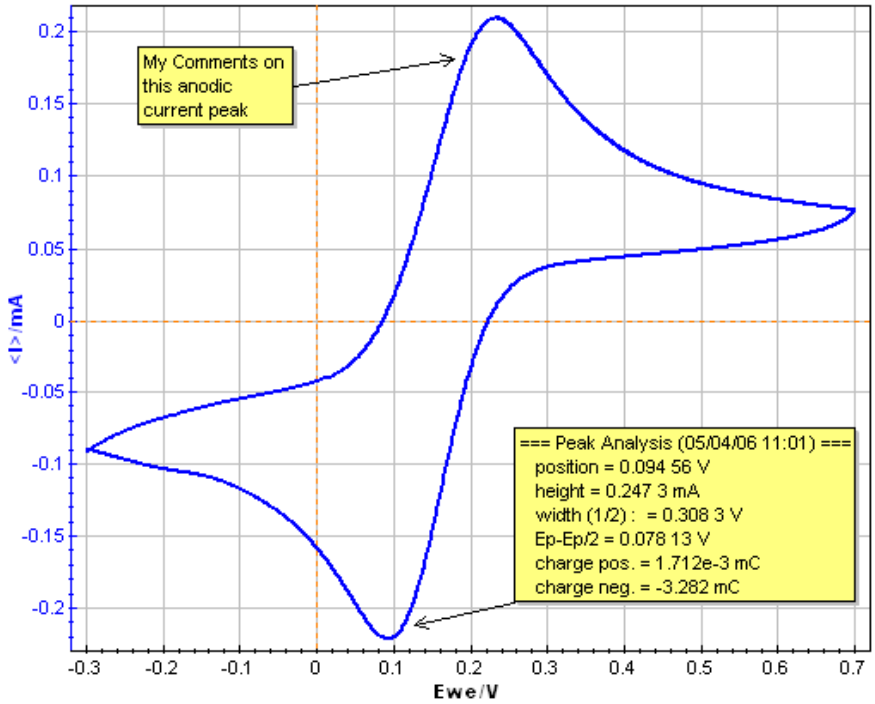


Fig. 77: Comment zones on the graph.

To add Comment zones on the graph the user must right click and select "**Add comments…**". Then an empty comment zone appears on the graph. To modify this zone, double click on it or right click on the zone and select "**Edit comments…**". The following window appears:

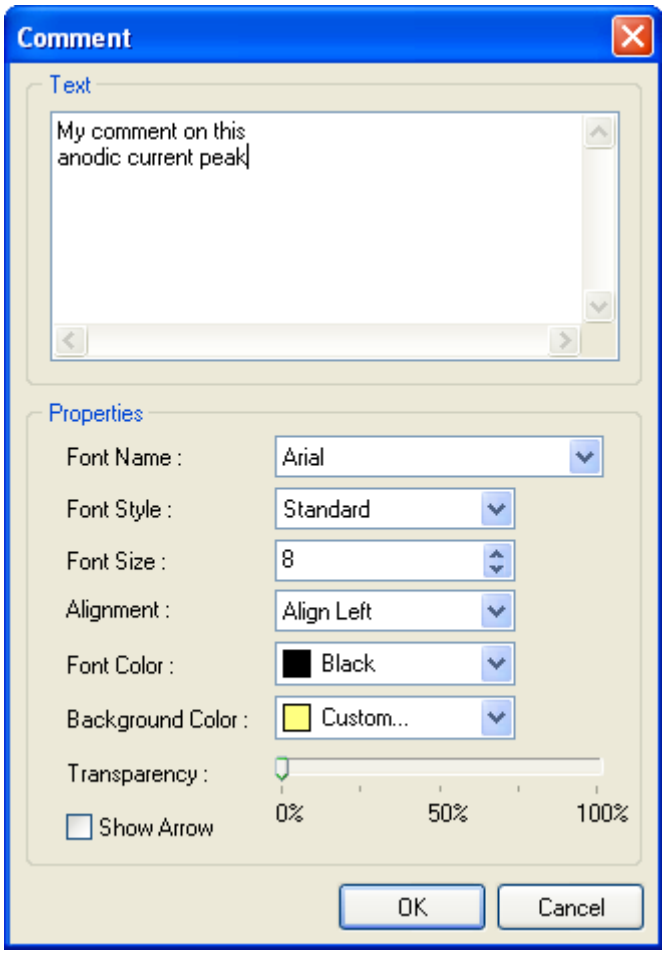


Fig. 78: Edit Comment zone.

The user can paste analysis results or other comments into the text frame. Several comment zone properties are available and the user can display an arrow and direct it through the desired part of the curve (by clicking on the end of the arrow).
To remove comment zones, right click on the zone and select “Delete comment” or click on the Del. keyboard button.
Note: The comment zone is automatically printed on the graph.

3.2.4 Three-Dimensional graphic

A 3D representation is available by right clicking on the graph menu. After clicking on the 3D menu, the Selector menu is available and allows to the user to choose the variables to display. An example of the Bode diagram obtained with the 3D representation tool is given Fig. 79.

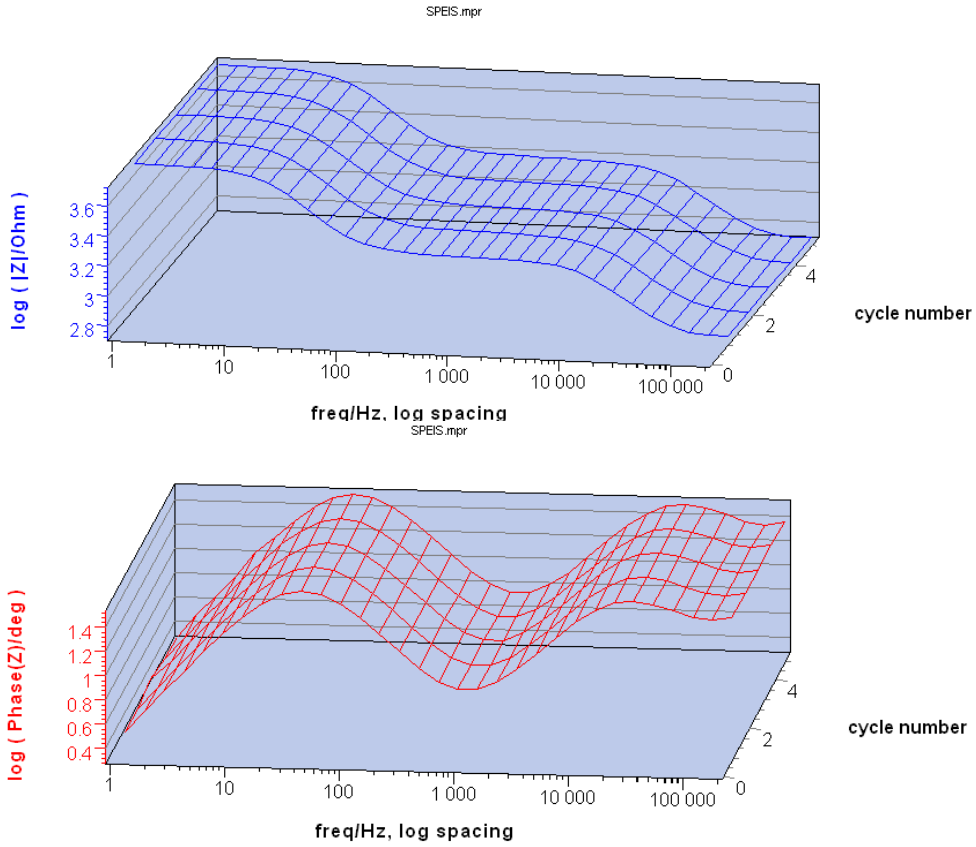


Fig. 79: Bode diagram obtained with the 3D representation.

Once on the 3D representation, it is possible to reach the 3D menu by right clicking on the graph (Fig. 80). Thanks to this menu, it is possible to come back to the 2D representation or to display simultaneously 2D and 3D graphs. As for the 2D representation, it is possible to Copy and Print the graph as explained in section 3.2.7 page 70. The Graph properties menu for the 3D representation is the same that the Graph properties menu for the 2D graph and this menu is detailed in the following paragraph.

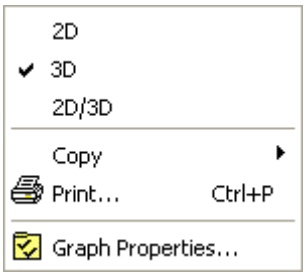
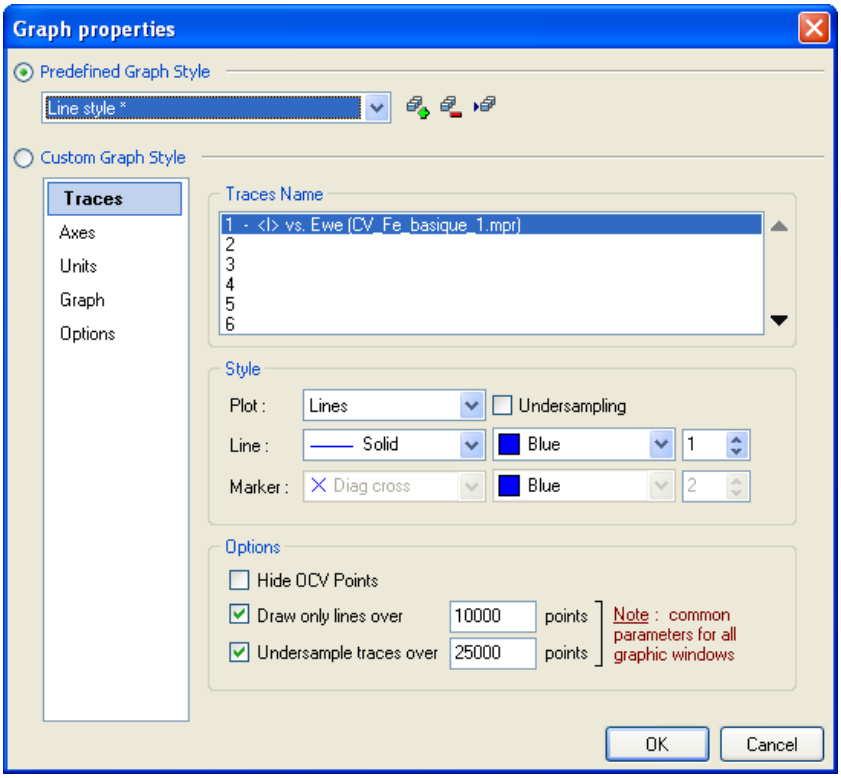


Fig. 80: 3D menu.

Note that to display a data file with the 3D function, the number of points should be inferior to 15000 points.

3.2.5 Graph properties

On the graphic window, right click on the mouse and select "**Graph properties**". This Graph properties window is divided into 5 themes: Traces, Axes, Units, Graph and Options. Each of them allows the user to define properties of the graphic display.



The Traces window allows the user to define all the properties of the selected traces. Select the trace you wish to modify in the Trace Name frame.
The available trace properties are
- the plot style: Line, Line+Markers, Markers,
- the line properties: solid, dash, …, color and size,
- the marker properties: rectangle, circle, …, color and size.
An undersampling option is available when lines are plotted (not with markers).

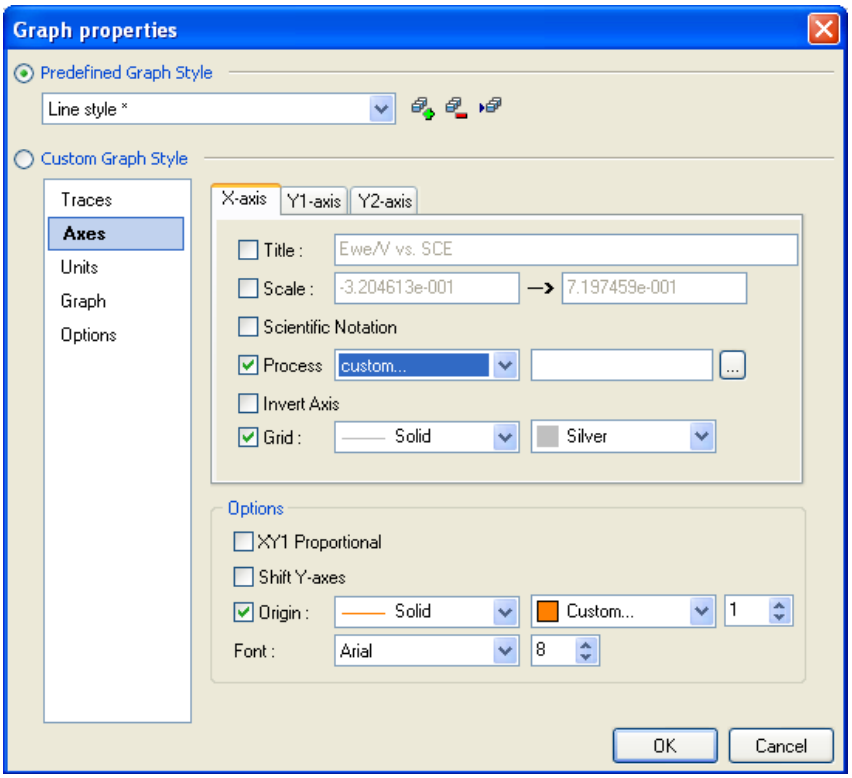
Fig. 81: Traces window.

In the Options window, it is possible to choose to hide OCV point or to draw only lines over a number of points or to undersample traces over a number of points. Note that the two last possibilities should be the same for all the traces.
Note: When several traces are plotted on the same graph the user can change the active trace with a left click on the desired trace (when the mouse becomes a hand with a pointed finger).
It is also possible to select between four styles already defined:

- Line style = only blue solid line,
- Line Markers style = blue line + circle markers,
- XY prop.style = blue line + circle markers and proportionality between X and Y axes,
- Monochromatic = black line. The other curves in this style will be in black with dash or dot lines. This style is specially dedicated to scientific articles.

Nevertheless, the user can define his own style defined with all the functions of the Graph Properties window (Traces, Axes, Units, Graph, Options).

Creation of a new graph style is possible with the button. This new graph style will be recorded automatically.

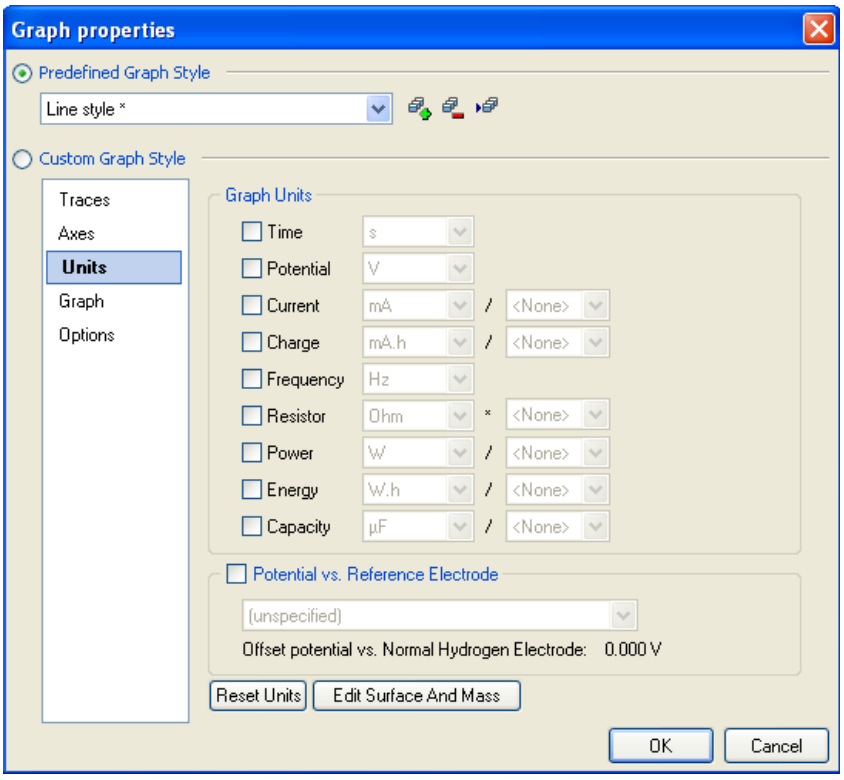


All the Axes properties can be changed in this tab. Select the axis you want to modify in the index tabs.
It is possible to change the title of the axis, but also to adjust the axis range to the user's convenience. The user can also change the notation to scientific mode or invert the axis (positive values on the left and negative values on the right).
The grids can be hidden while deselecting the box. The user can choose the color and the style of the grid.

Fig. 82: Axes window.

In the option part, the user can choose to display his data with the X and Y axes proportional (generally used for Nyquist representation) and to differentiate from the rest of the grid the axis origin (color, style or line size).
The font type and size is also available from this option menu.

Note: - On the graph the user can move one of the Y axes with the mouse (left click) in order to adjust the origin of both Y axes. Put the mouse on the axis to see the and move the axis.



Graph Units window is used to choose the correct graph units for the different variables.
The default units are in gray boxes. If the user chooses another unit, he must activate his choice by ticking the box corresponding to the represented variable. Specific units are available for current and charge on one hand and for power and energy on the other hand. For current and charge, the user can select a current density or a charge density according to the electrode area or to the electrode characteristic mass.

Fig. 83: Units window.

Power and energy can be plotted according to the electrode characteristic mass. In such a case the software will ask for the electrode surface area or for the characteristic mass. The following windows will be displayed:

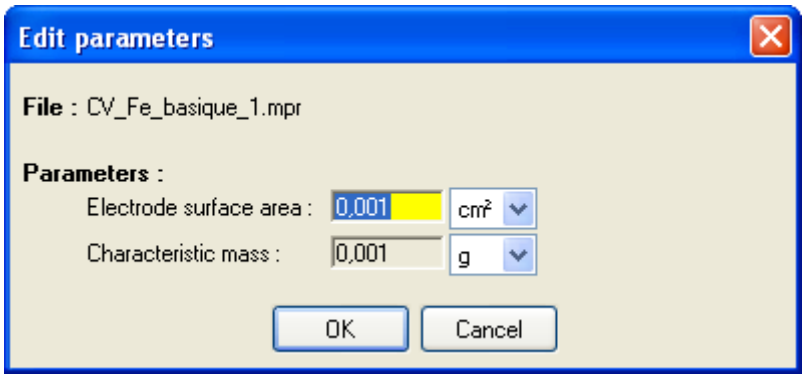


Fig. 84: Electrode Surface Area and Characteristic Mass window.

The Electrode Surface area and Characteristic Mass window is used in the unit window for area charge or current density plot. The characteristic mass is also used for specific power or energy plot. The user has to set the working electrode surface area/characteristic mass and choose the unit. Clicking **OK** will modify the graph according to the new surface but this area is not saved in the raw file. Click on **Save to file** to save the surface in the raw data file.

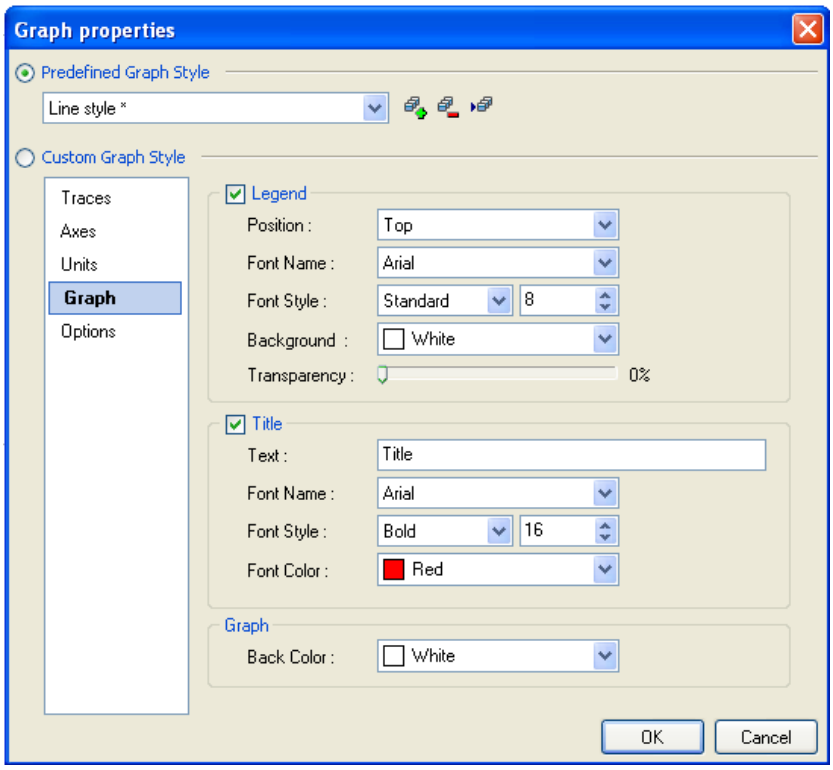


Fig. 85: Graph window.

The user can show or hide the graph legend. He can define the position, the font name, style and size, the background color and the transparency of this background. The legend includes the file name.
Note: When several traces are plotted on a graph, the user can select the active trace by clicking on the corresponding legend.
A title can be added to the graph to describe the experiment. The text must be typed in the box. The user can choose the title's format (font, font style, size and color).
To improve contrast and legibility for a presentation for example, the user can change the color of the graph background.

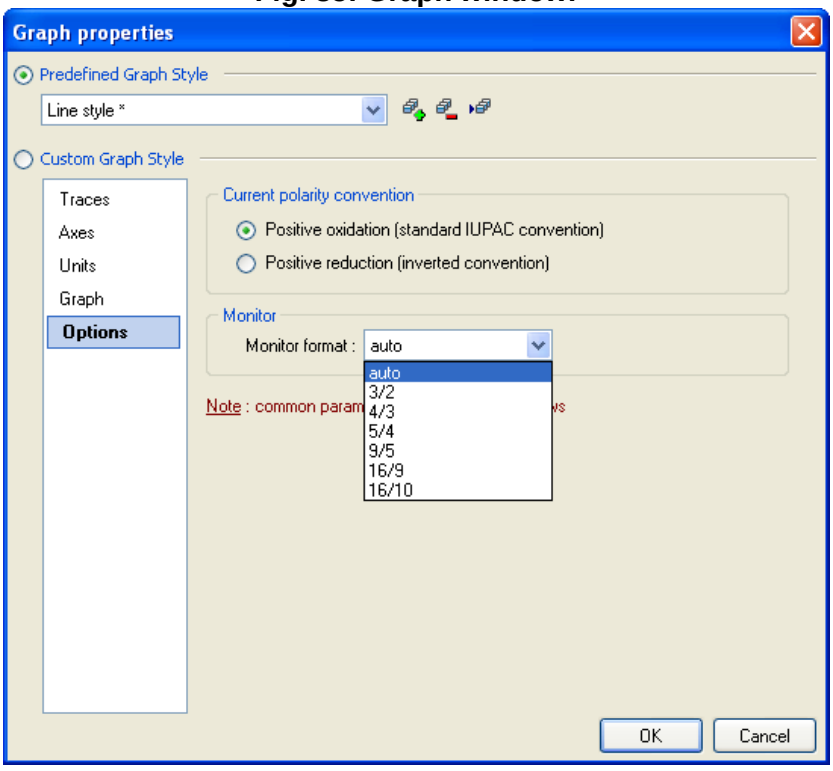


Fig. 86: Options window.

This window allows the user to select the current polarity conventions to display data files

- The standard current convention from IUPAC with a positive value for the oxidation current.
- The inverted current convention with a positive value for the reduction current.

It is also possible to adjust the graph size to the monitor format.

3.2.6 The LOG (History) file

The log file summarizes all parameters used for an experiment (with the possible modifications on-line). Log displays the history of the experiment from its beginning.

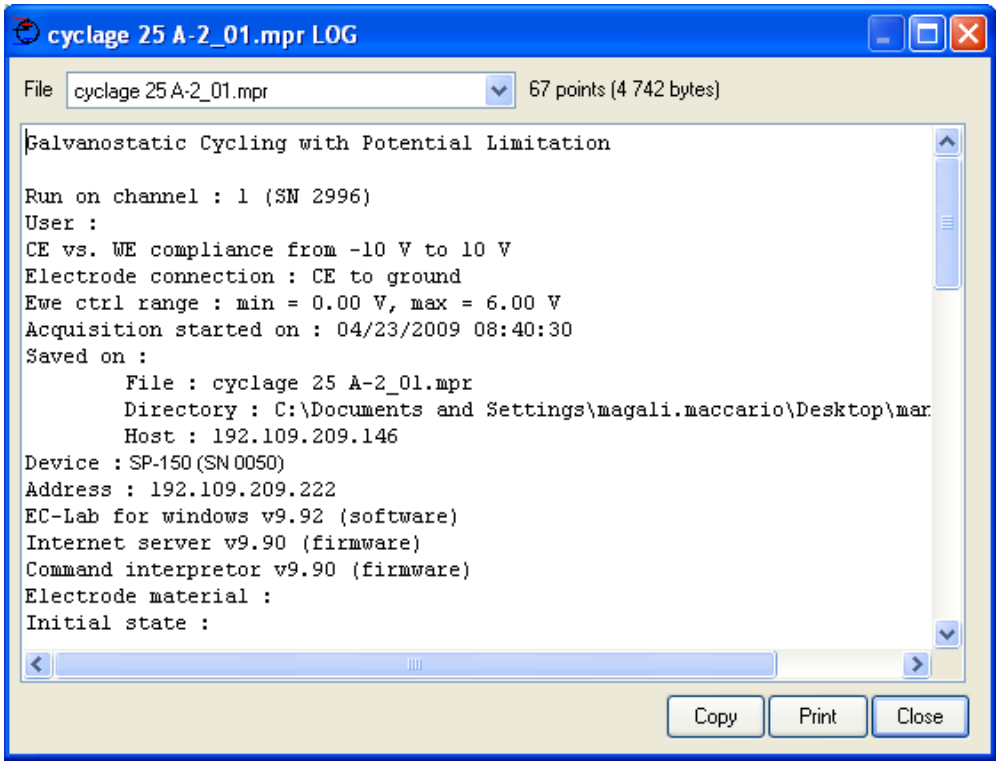

cyclage 25 A-2_01.mpr LOG
File
cyclage 25 A-2_01.mpr
67 points (4 742 bytes)
Galvanostatic Cycling with Potential Limitation
Run on channel : 1 (SN 2996)
User :
CE vs. WE compliance from -10 V to 10 V
Electrode connection : CE to ground
Ewe ctrl range : min = 0.00 V, max = 6.00 V
Acquisition started on : 04/23/2009 08:40:30
Saved on :
File : cyclage 25 A-2_01.mpr
Directory : C:\Documents and Settings\magali.maccario\Desktop\mar
Host : 192.109.209.146
Device : SP-150 (SN 0050)
Address : 192.109.209.222
EC-Lab for windows v9.92 (software)
Internet server v9.90 (firmware)
Command interpretor v9.90 (firmware)
Electrode material :
Initial state :
Copy
Print
Close

Fig. 87: Experiment history window.

The parameter modifications while the experiment is running are added to the end of the file. The number of points and the file size are displayed on the top of the window near the file name.

3.2.7 Copy options

On the graphic display several copy options are available. When the user right click on the mouse the following copy options can be found in the "**copy**" menu:

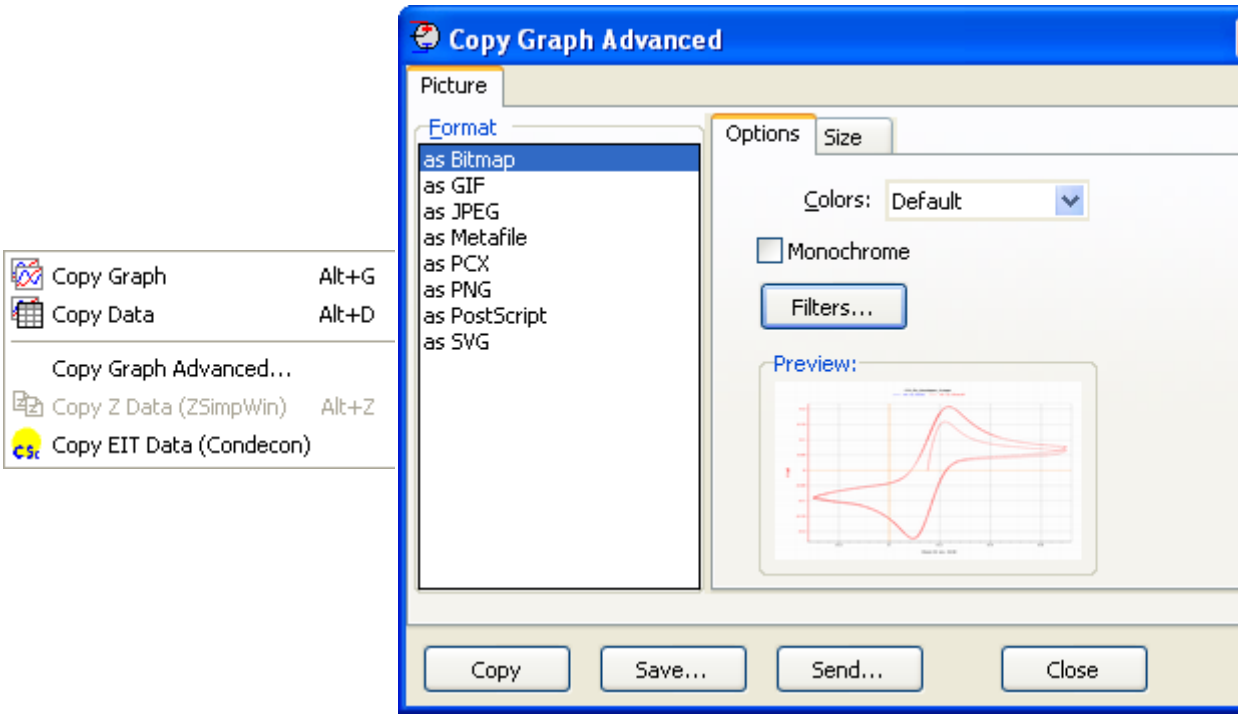


Fig. 88: Copy option and copy graph advanced menu.

3.2.7.1 Standard copy options

On the top of the menu two standard options permit copying either the graph or the data. The "**Copy Graph**" option will copy the graph to the clipboard as displayed on the computer screen in an enhanced metafile format (*.emf). The user can paste the file in the software he wants. The "**Copy Data**" option will copy the data selected on the graph (if data points are selected) or data as they are displayed on the screen in a text format in two columns with X and Y only. Data can directly be pasted in spreadsheet software.

3.2.7.2 Advanced copy options

Three advanced copy options are also available.

- The "**Copy Graph Advanced…**" option offers seven different file formats for the graph copied: enhanced metafile, Bitmap, SVG, Post Script, PCX, GIF and JPG with a possibility to choose the size of the picture in pixels.

- The "**Copy Z Data (ZSimpWin)**" option is a gateway to ZSimpWin® software. This copy option is only available with impedance data files. Three data rows (frequency, Re(Z) and Im(Z)) are copied in the ZSimpWin format and can be pasted by the user in this software. If the impedance experiment is repeated several times, only the displayed cycle is copied.

- The "**Copy EIT Data (Condecon)**" option is a gateway to Condecon® software. This copy option is available only with data files including potential, current and time. Three data rows are copied to the clipboard in the following order E, I, and t. this option only copies the data points corresponding to the displayed points on the graph.

3.2.8 Print options

Print displays the print window. The user can print only the graph. He can also choose to print the log file and some comments added by the user in the comments tab. All will be printed on the same paper page. The printer setup is also available with the setup button. A print preview is available to see the different parts of the page.

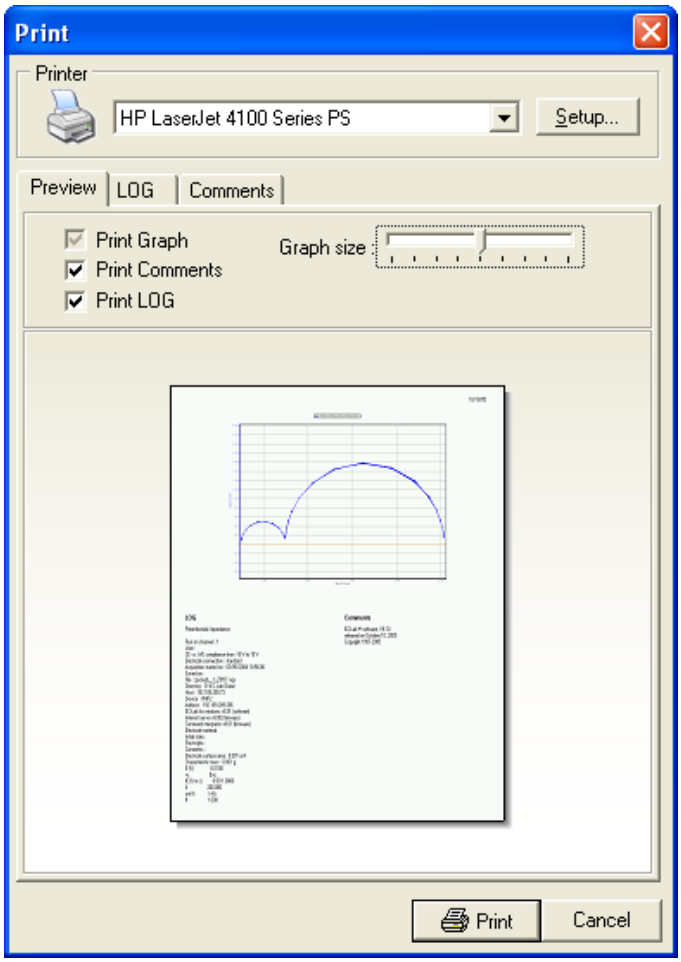


Fig. 89: Print window.

Note: the date is displayed and printed automatically in the top right corner.

3.2.9 Multiple graphic windows

3.2.9.1 Multi-graphs in a window

The EC-Lab® software graphic window is capable of displaying several different and independent graphs. Four graphs can easily be displayed in the same window.

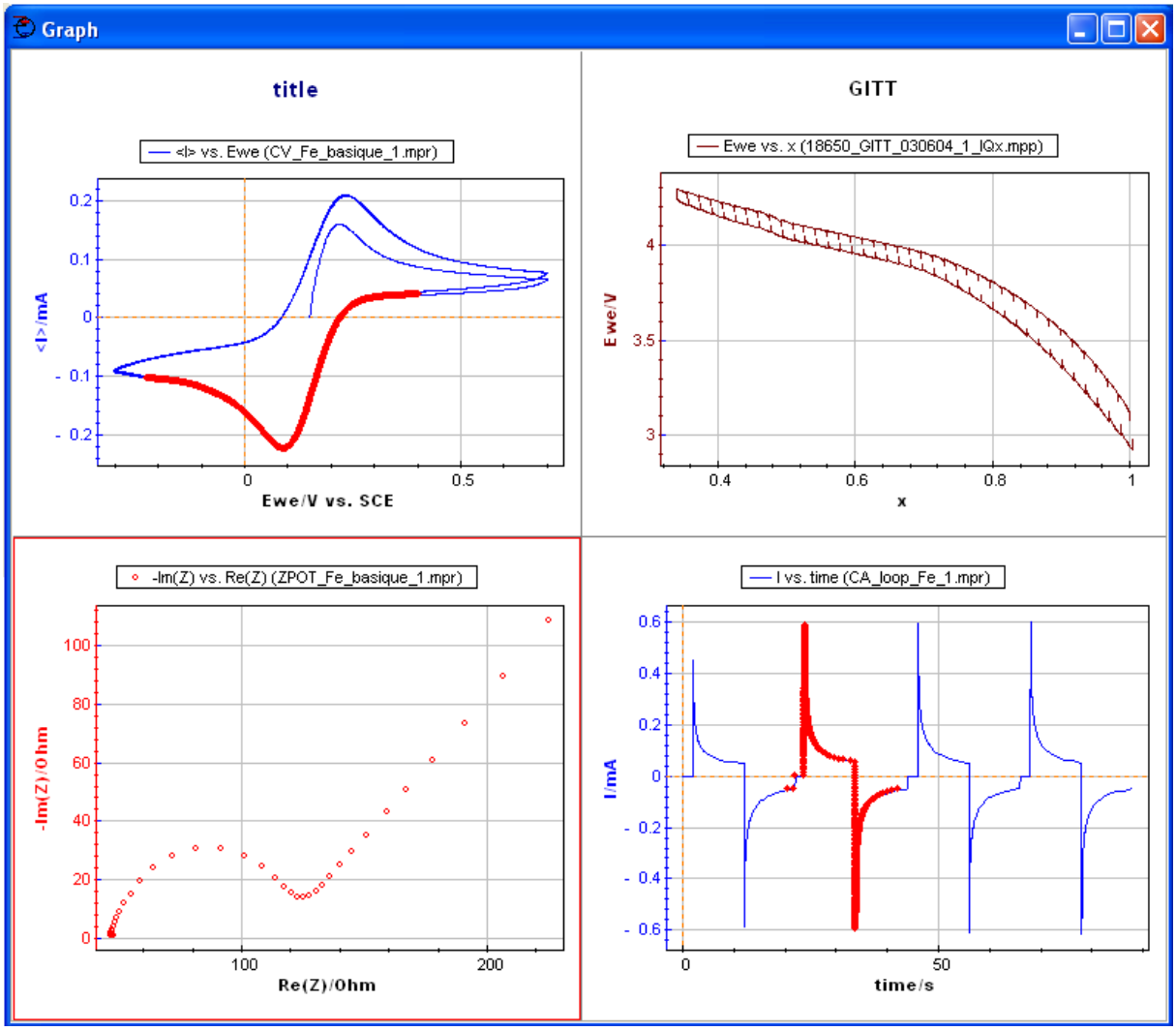


Fig. 90: Multigraph window.

To display several graphs on the same window, right click on the graphic window, select "**Add Graph…**" and choose the data file to display. One graph is active on the window (with a red frame in the left bottom corner). The other graphs are not. In the multigraph mode fits and analysis remain possible on the active trace of the active graph. The graph properties can be modified for each graph independently.

3.2.9.2 Multi windows

When several windows are displayed in the EC-Lab® software the user can either show windows in cascade or tile the windows on the screen. Choose **Windows, Tile** to display several graphic windows at the same time.

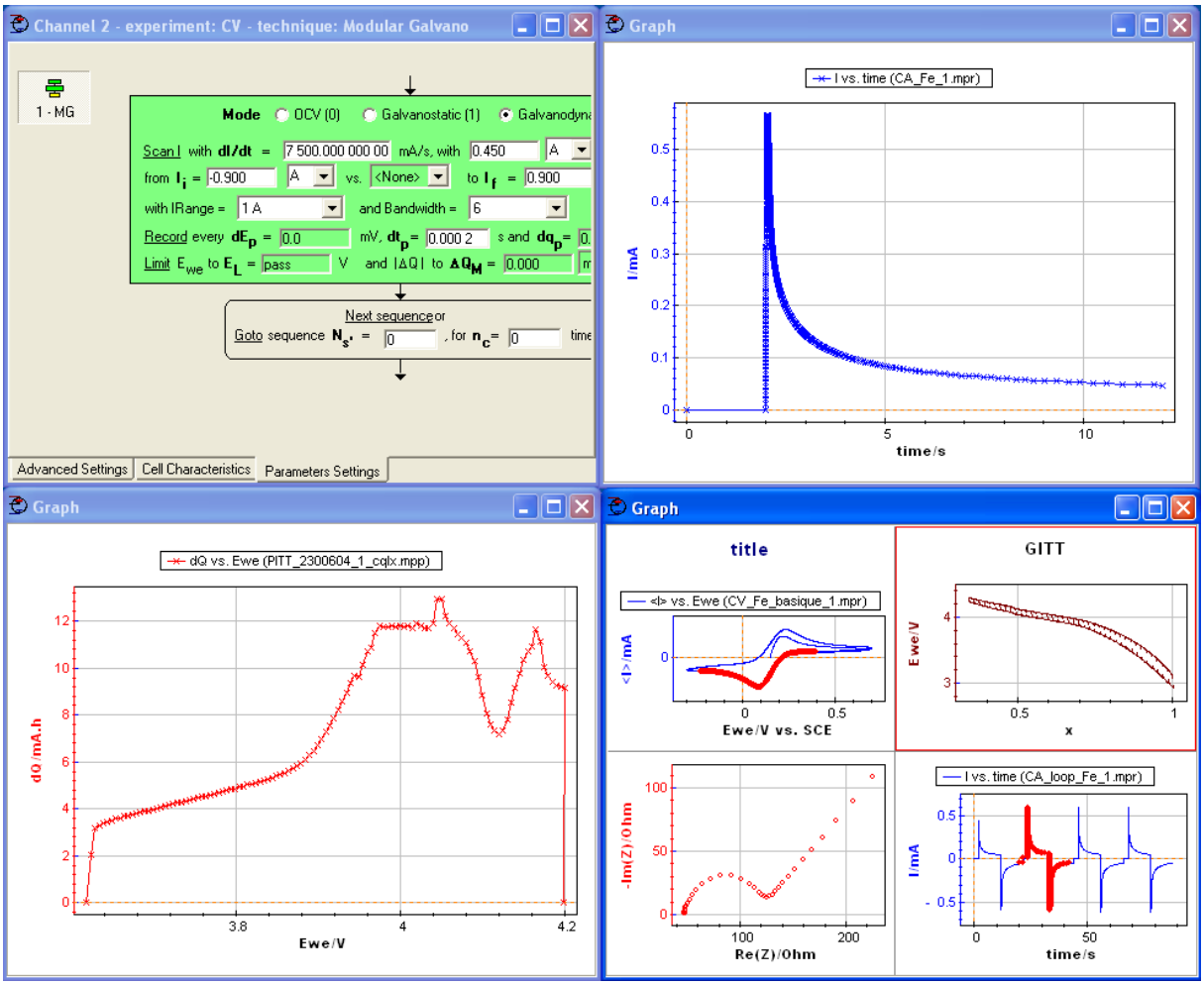


Fig. 91: Multi-windows.

This can lead to a very complex displaying mode that may be very useful for multichannel display.

3.2.10 Graph Representation menu

It is possible for the user to define fast graphic displaying modes with the Representation tool in the Graph menu.

The **Graph Representations** window already offers some standard representations. For each representation, a scheme of the axes is given. For example, in the Fig. 92, the Bode impedance representation is given. This representation is defined as:

- the frequency value on the X axis. This value is processed with the log spacing function,
- the IZI value on the Y1 axis. This value is processed with the log function,
- the Phase(Z) value on the Y2 axis.

It is possible to display the two Y axes on the same graph or to separate them selecting the “Separate traces” box.

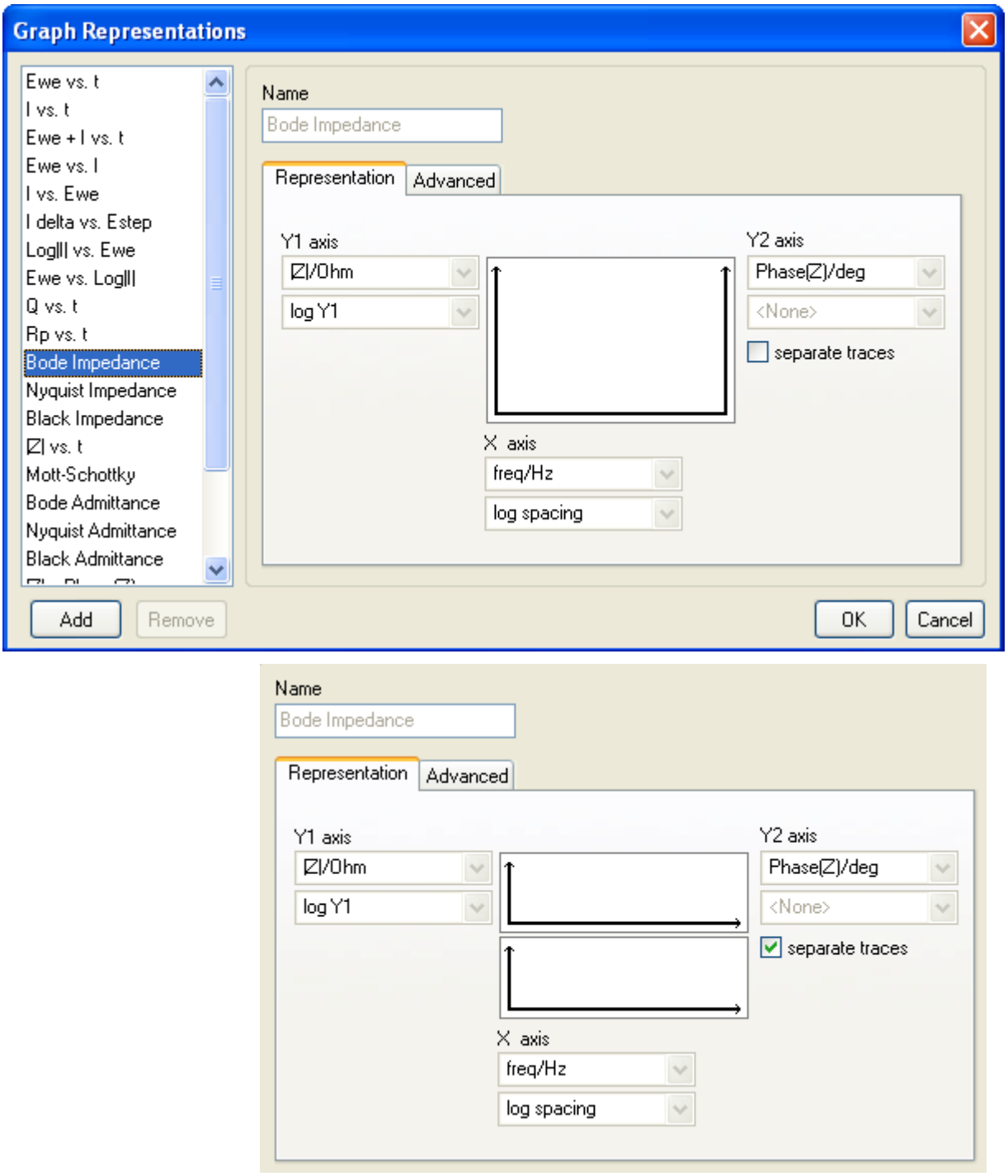


Fig. 92: Graph representations window.

3.2.10.1 Axis processing

As shown previously, it is possible to apply a mathematical function on each axis. By default standard functions such as log X, -X, |X|, 1/X are proposed (Fig. 93). Nevertheless it is possible for the user to define his own processing function using the **Custom** menu.

Then in the window given Fig. 93, the user can define an operation in the Variable box (in this example it is the x box). Mathematical functions are available ticking the box more.

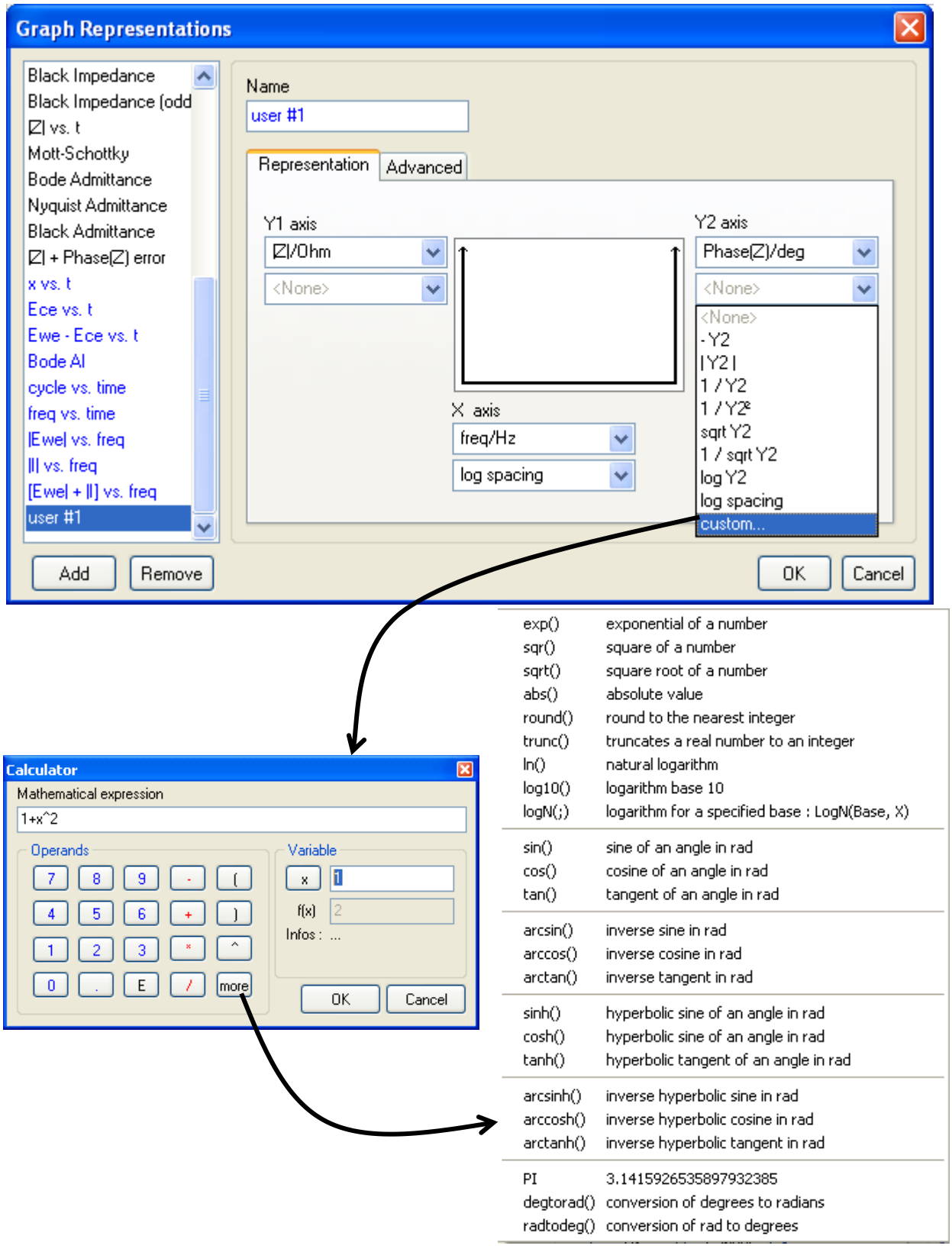


Fig. 93: Axis processing window and available mathematical functions.

3.2.10.2 How to create your own graph representation for a specific technique?

To facilitate data treatment, it is possible to create a specific representation for each technique. For this, the user has to click on "**Add**" in the bottom of the **Graph Representations** window; then a "**User #x**" variable is automatically created. The user can change the name of the display. He must select variables to be displayed on X-axis and on Y1 and Y2 axes in the **Representation** window. He can also define a processed display for each axis in the **Advanced** window.
Once definition of each axis done, it is possible for the user to define the Graph style but also the techniques to which apply this process. The selection of the Graph Style can be done on the **Advanced** menu as shown in Fig. 94. As mentioned in the Graph properties part the user can choose amongst four available **Graph Styles** or define himself a Graph Style that can be associated with defined techniques. This can be done selecting the **Edit** menu, see following paragraph for more details about the Graph Style creation.
Clicking on the second **Edit** button does the technique selection. Once the selection done, techniques are displayed in the Selected techniques box as shown in the Fig. 94.

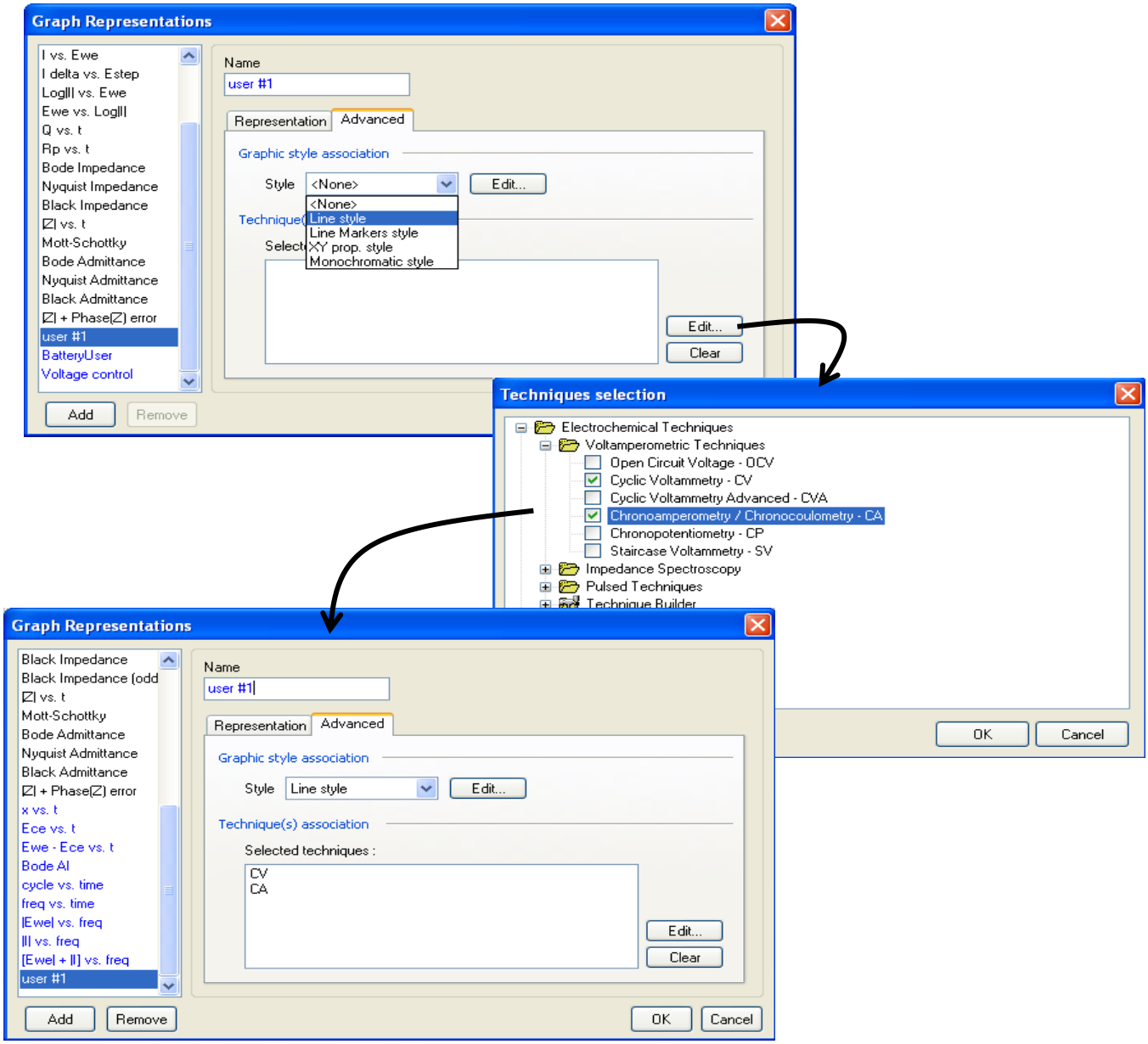


Fig. 94: Graph Style and technique selection.

Note: this graph representation will only be available if the variables to display are recorded in the current .mpr file for which the representation will be applied.

3.2.10.3 How to create a Graph Style?

It is often convenient to display the obtained data with the same way: same trace color, same markers, same units …. For this, it is possible with EC-Lab® to create a Graph Style. In the **Graph** tab, select the **Representations** menu. The **Graph Representations** window will be displayed, in this window select the **Advanced** tab and the four already predefined Graph Styles will be displayed (Fig. 95). To define your own Graph Style, click on the Edit... button, the window **Graph Properties** will be displayed as shown Fig. 96.

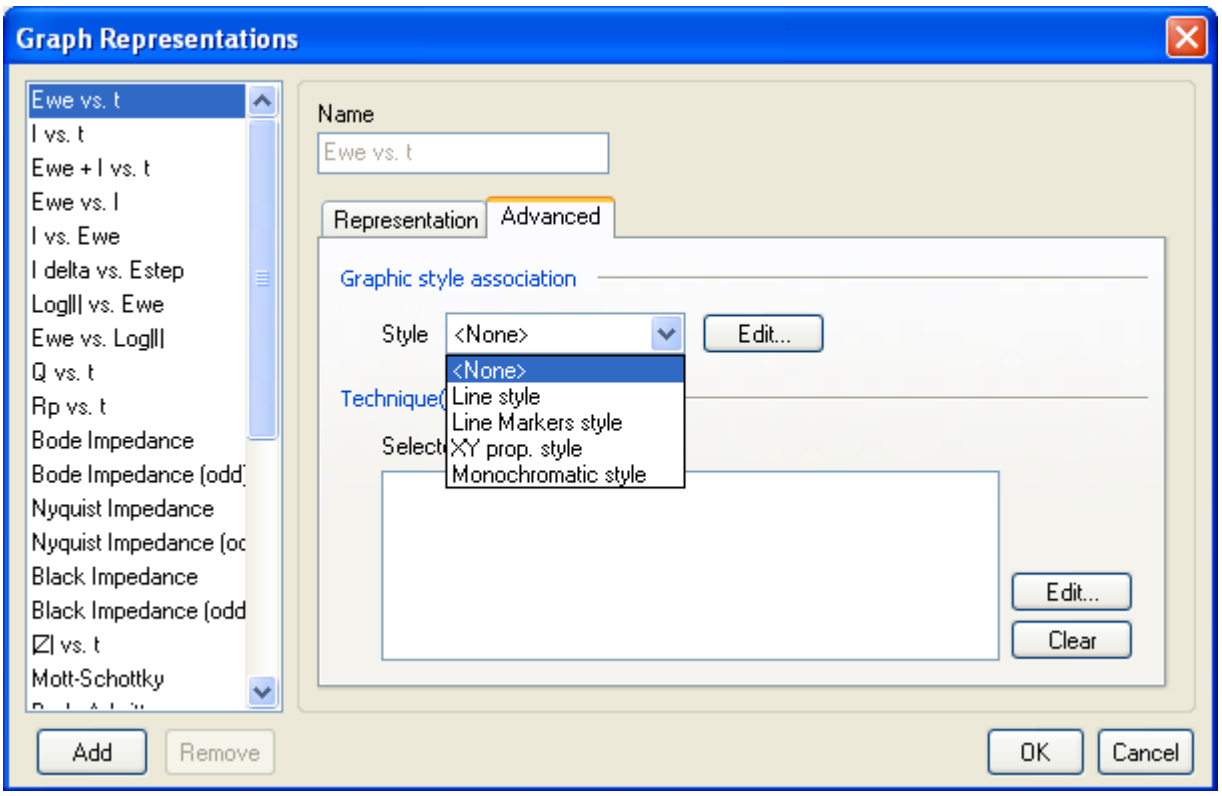


Fig. 95: Graph Style selection.

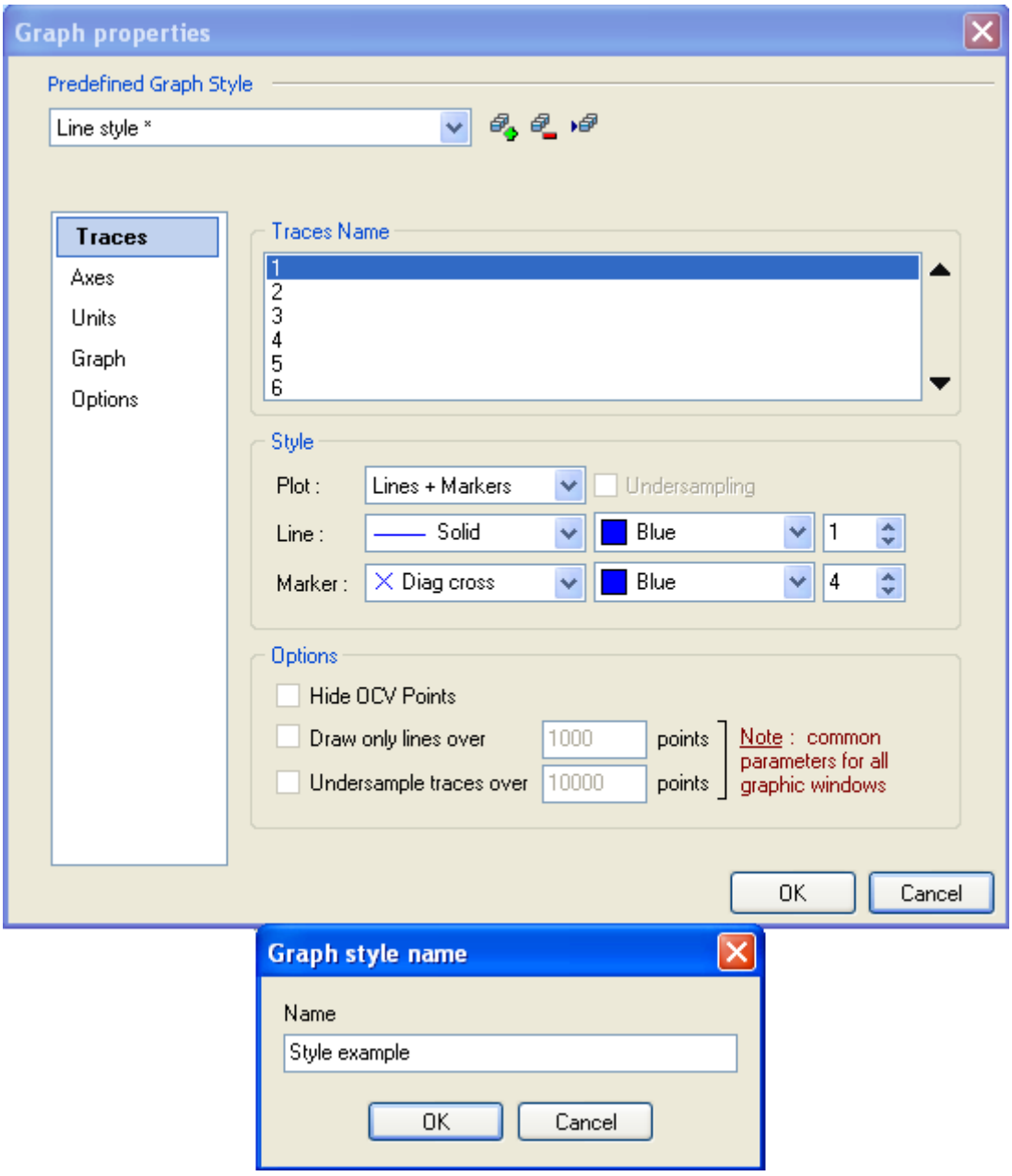


Fig. 96: Graph Properties window in the Graph Style creation.

When clicking on the button, a Graph Style name window appears, then the user can choose the name of the new Graph Style. For this example, a Graph style named “Style example” is defined in such a way that the curve 1 is defined as red solid lines and fushia triangles marker and the curve 2 is defined as blue solid lines and blue sky diag cross marker (Fig. 97).

The Graph Style definition includes all the graph properties, these properties were previously defined in the section 3.2.5.

Once the definition of the Traces, Axes, Units, Graph and Option done, user has to click on **OK** and the new graph style is added to the Graph Style list.

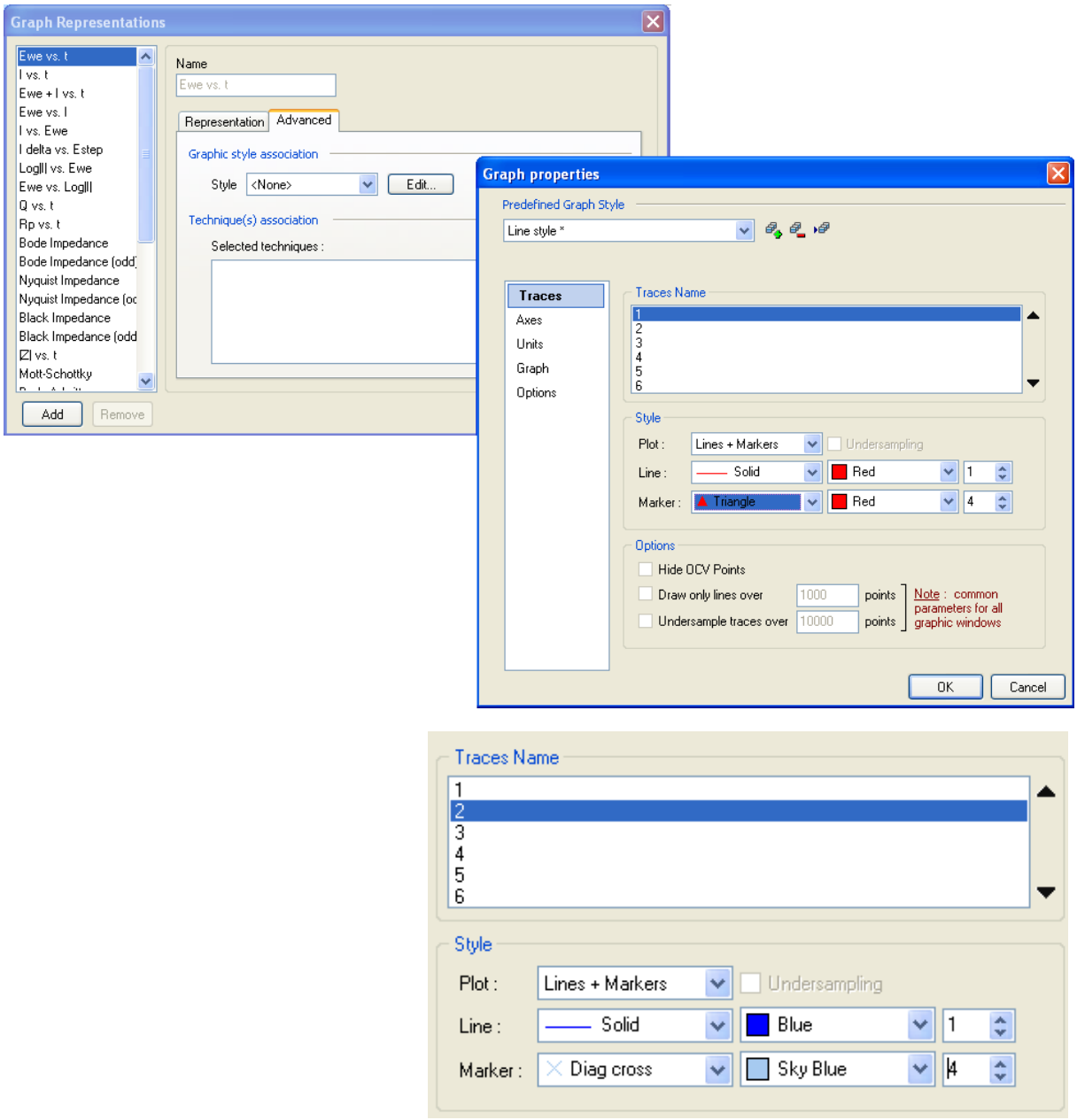


Fig. 97: Definition of traces properties in Graph style definition.

3.3 Graph Tools

The EC-Lab® software contains powerful graphic tools. It is possible to perform, **Linear** Fit, **circular** Fit, **R_p** Fit, **Tafel** Fit, **Integral** calculation, **Min and Max** determination, **peak analysis**, **wave analysis** in convective regime, **Linear Interpolation**, **ZFit**, **Fourier Transform**, **Corrosion simulation** (Corr. Sim.), **Filter**, Constant or Variable amplitude Sinusoidal micro Polarization (**CASP Fit** or **VASP Fit**) and **Mott-Schottky** Fit within the Graphic display. These analyses are available in the Analysis menu and the right click menu (as described above). They will be described below.

First of all, before any analysis, select the trace to fit (if several traces are displayed on the graphic window) or the cycle (if a trace contains several cycles). There are two different ways to make a fit on a trace with the EC-Lab® software. Two steps must be considered: the zone selection and the fit choice. One can be made before or after the other. The two ways to proceed are as follows:

1) In the main tool bar click on "**Graph**" and then "**Selection**" or click directly on the selection button of the graphic tool bar. On the graphic window select the zone, which needs to be analyzed by holding the left mouse button. The cursor will draw a rectangle around the chosen zone. Once it is complete, release the mouse button. The part of the curve selected should be highlighted in red and ready for analysis. Then select the required analysis either with the right click menu or in the "**Analysis**" menu or in the graphic toolbar.

2) In the Analysis menu or in the graphic tool bar select one of the tools. The mouse selection mode is automatically selected. The user has just to start a zone selection as described above.

Now a zone is selected on the trace and a fit window is displayed.

3.3.1 Zone selection

On the graphic display the zone selection can become very complex when several cycles or loops have been made during the experiment or when several zones are selected at the same time. In such a case, the software will ask you to select only one trace before doing a fit.

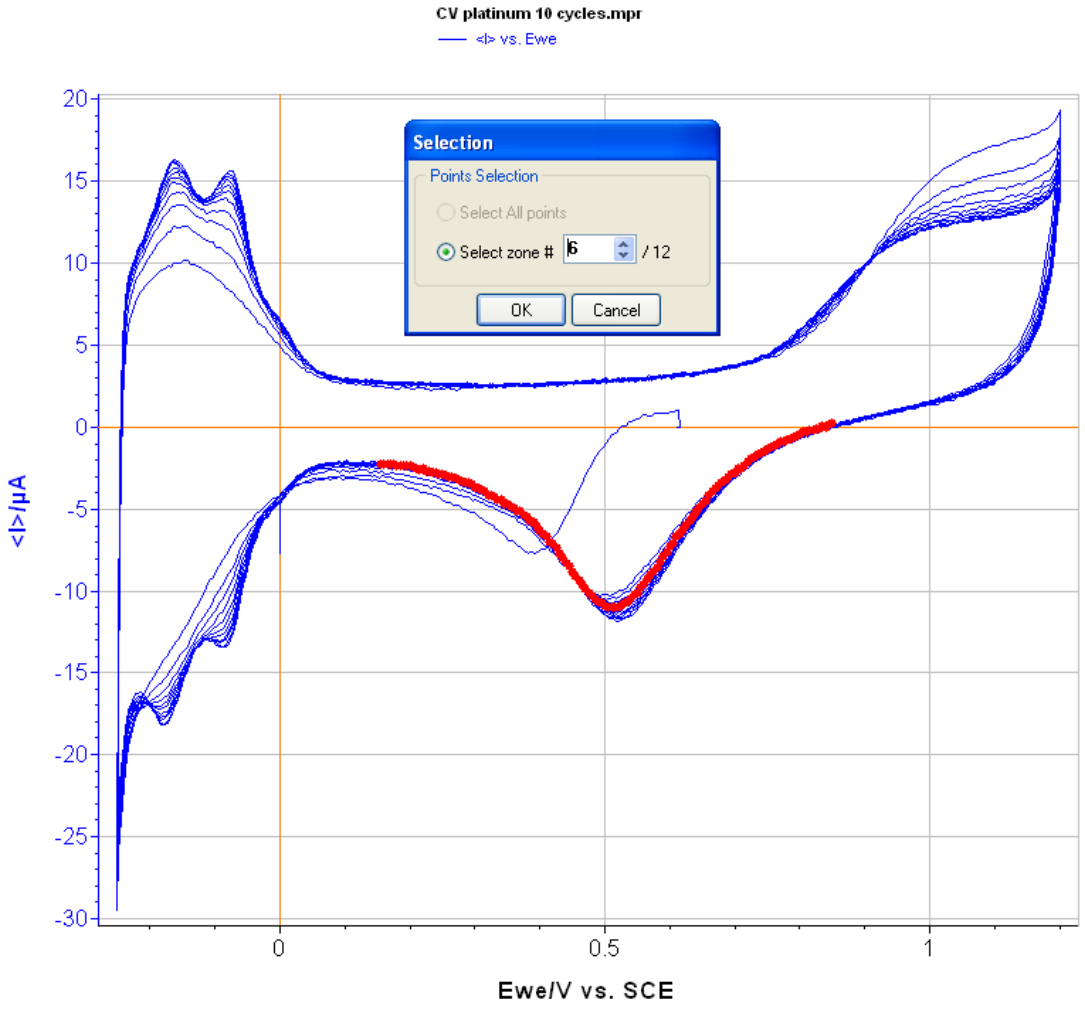


Fig. 98: Zone selection on the graph

In this example, the user can show one cycle (right bottom corner). In that case he will be able to select only one trace. If several discontinued traces are selected in the zone, the selection window is displayed to choose one trace for the fit. Select the zone and click **Ok**.

3.4 Analysis Menu

The analysis menu is separated in six analysis sections depending on the application: Mathematic, General electrochemistry, EIS, batteries, photovoltaic/fuel cells and corrosion

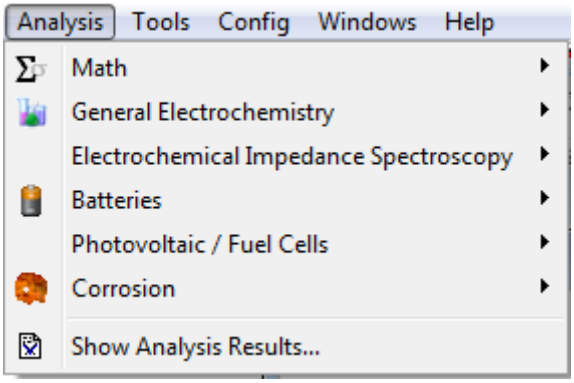


Fig. 99: Analysis menu

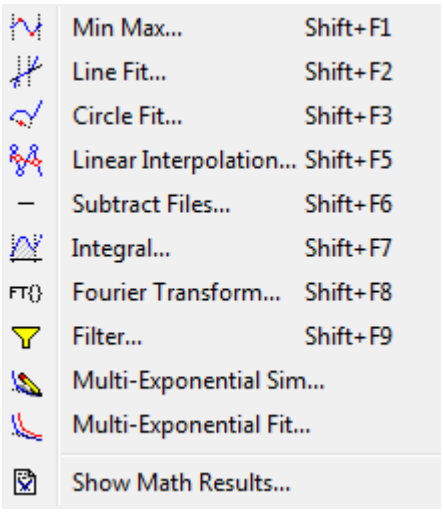


Fig. 100: Math Menu.

The Math menu contains the Linear and the Circle fits, but also the determination of the minimum and the maximum on a curve. This Math menu allows also the user to filter the obtained curve, to substract curves, to do Integral on parts of the curve or to do a FFT transformation.

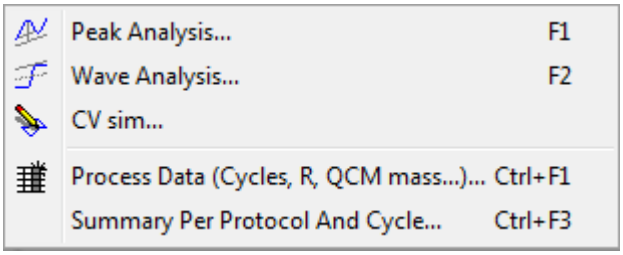


Fig. 101: General electrochemistry menu.

In this menu, the Peak and the Wave analysis are available but also two processes to determine for example R or the cycle number.

Fig. 102: EIS menu.

This menu is especially dedicated to the analysis of EIS data. It is possible to simulate various EIS diagrams with ZSim tool, or to fit with various electrical circuits an existing diagram with ZFit tool.

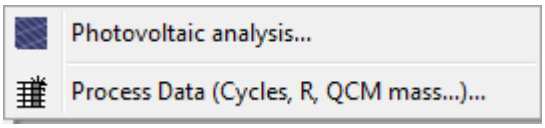


Fig. 104: Photovoltaic/fuel cell menu.

This menu provides analysis tools for experiments done on photovoltaic components and fuel cells.

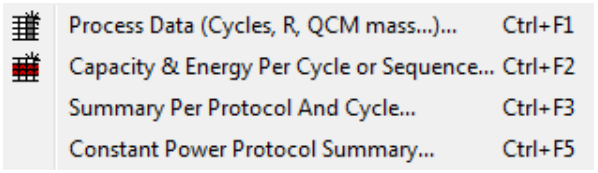

Process Data (Cycles, R, QCM mass...)... Ctrl+F1
Capacity & Energy Per Cycle or Sequence... Ctrl+F2
Summary Per Protocol And Cycle... Ctrl+F3
Constant Power Protocol Summary... Ctrl+F5

Fig. 103: Batteries menu

The Batteries menu is composed of processes allowing the user to add some variables, such as x, capacity during charge, energy, … to his file or to calculate for each cycle the capacity and the energy values, to summarize all the significant parameters obtained during each cycle.

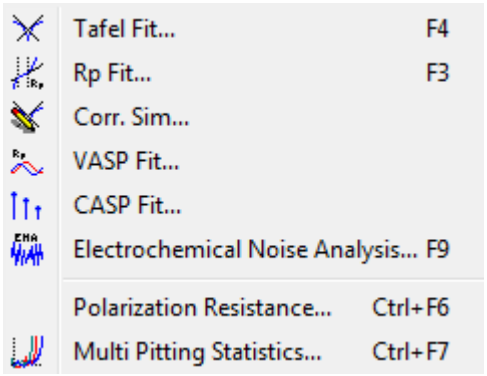


Fig. 105: Corrosion menu.

This menu contains the classical corrosion tools such as Rp Fit and Tafel Fit, but also a tool to simulate corrosion curves, an analysis of electrochemical noise and two tools to determine easily and quickly current and coefficients of corrosion. Moreover two dedicated processes are available.

3.4.1 Math Menu

3.4.1.1 Min and Max determination

On the graphic display, select **Min/Max** with the Min/Max button or the mouse right click and the data points where the fit will be performed. The Min/Max analysis window appears. Select the zone to fit on the trace and click on "**Calculate**". The Min and Max values are automatically detected.
The Min and Max coordinates are displayed in the fit window and highlighted in red on the trace.

The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

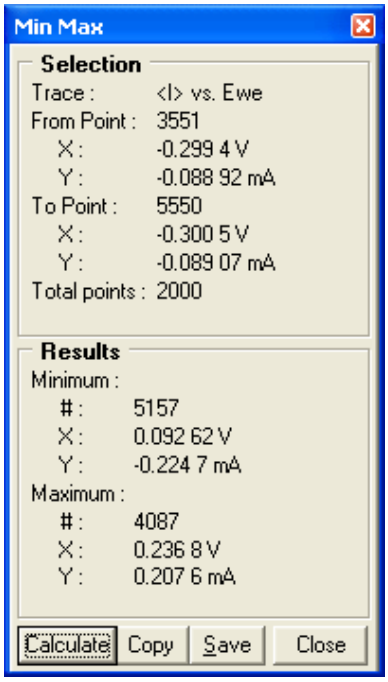


Fig. 106: Min/Max fit window.

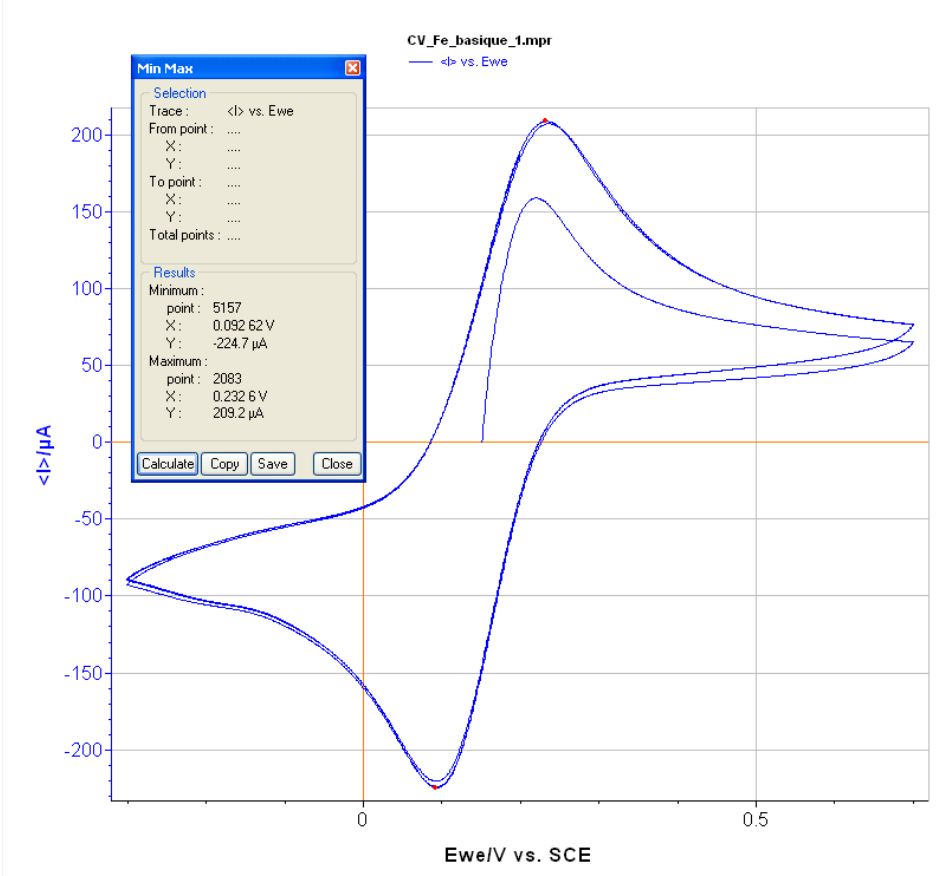


Fig. 107: Min/Max determination on the graph.

3.4.1.2 Linear Fit

When the zone to fit is selected click on "**Calculate**" in the linear fit window (Fig. 108). A straight line is displayed as a result of the linear regression between two green circles with the Least square method fit (Fig. 109).

Move the circles with the mouse (by holding the mouse left button) to modify the range of data points selected for the fit. The new linear regression is automatically calculated when one of the circles is moved.

The coordinates of the first and last data points used for the fit are displayed as well as the number of points used for the fit in the **Selection** frame.

The results can be copied to the clipboard to be pasted in the print window comment zone or in a text file. They can be saved in a text file.

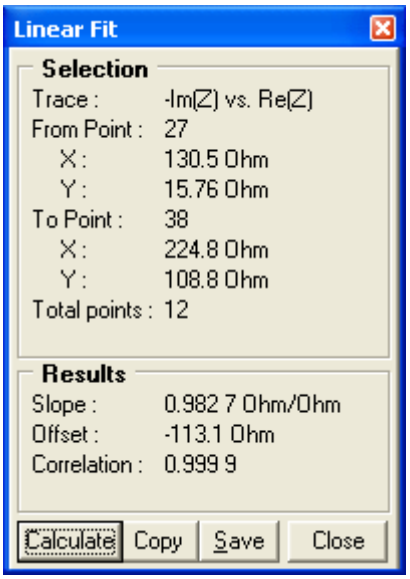


Fig. 108: Linear Fit window.

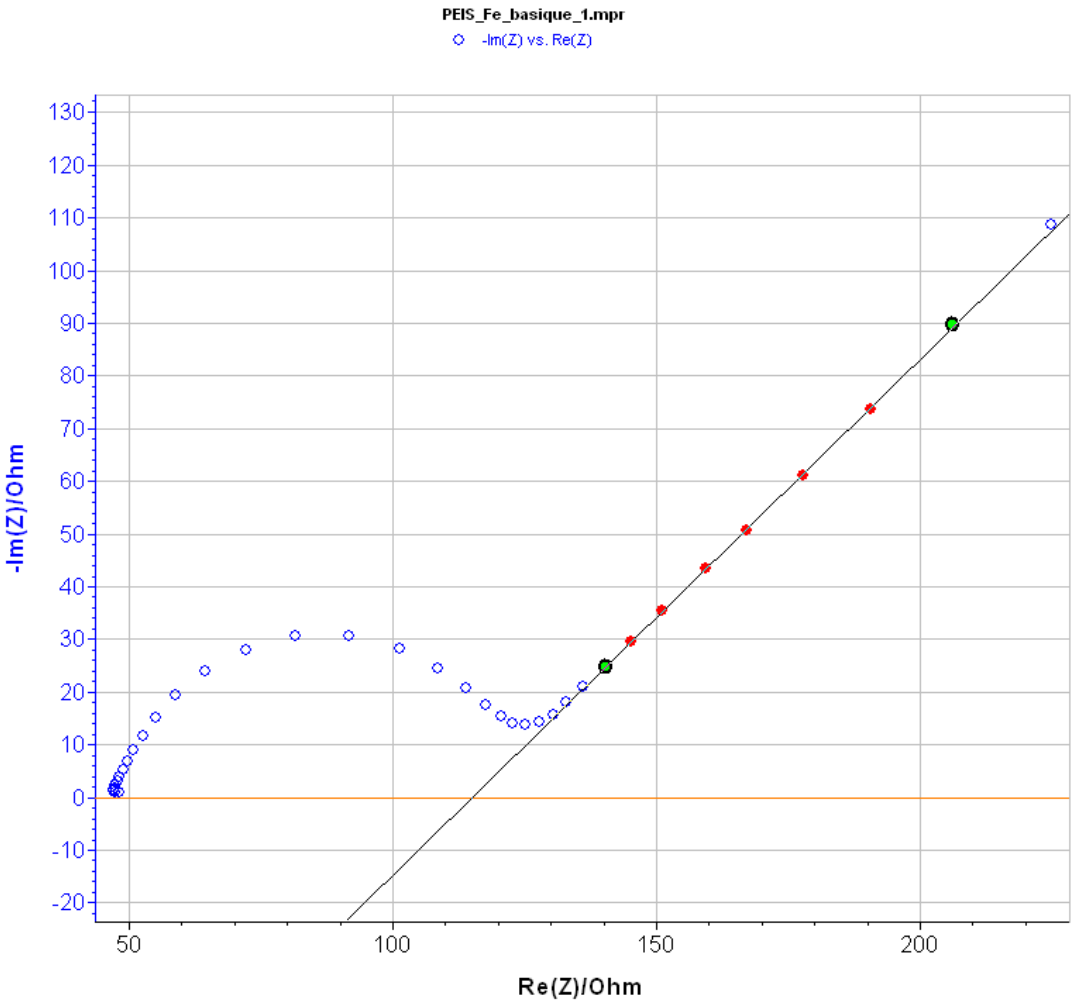


Fig. 109: Linear Fit on the graph.

3.4.1.3 Circle fit

When the zone to fit is selected click on "**Calculate**" in the circular fit window (Fig. 110). A part of a circle curve is displayed as a result of the regression between two green cursors with the Least square method fit (Fig. 111).

Move the cursors with the mouse (by holding the mouse left button) to modify the range of data points selected for the fit. The new regression is automatically calculated when one of the cursors is moved.

The coordinates of the first and last data points used for the fit are displayed as well as the number of points used for the fit in the **Selection** frame.

In the **Parameters** frame, an iterative algorithm allows the adjustment of the results using a minimization with the simplex method.

The results displayed are the parameters of the circle. The depression is the angle between X-axis and the diameter defined from low x-intercept. R is the difference between high x-intercept and the low x-intercept. C is the capacitance determined for the experimental point in the selected zone where –Im(Z) is max ($Rc\omega = 1$).

The parameters and results can be copied to the clipboard to be pasted in a comment zone, the print window, or a text file. They can be saved in a text file.

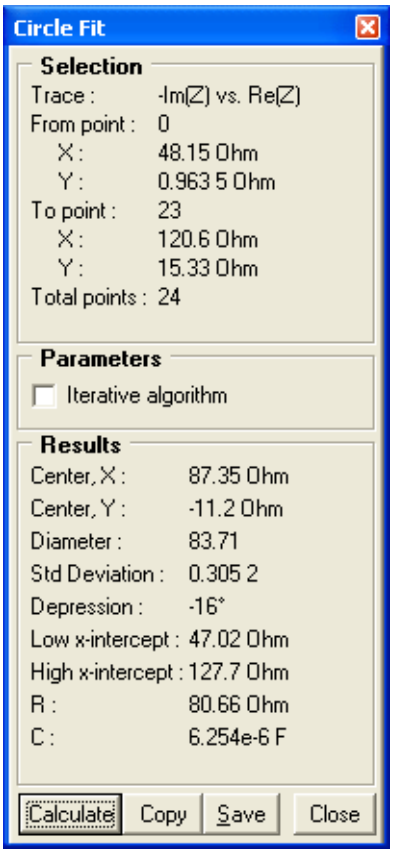


Fig. 110: Circular Fit window.

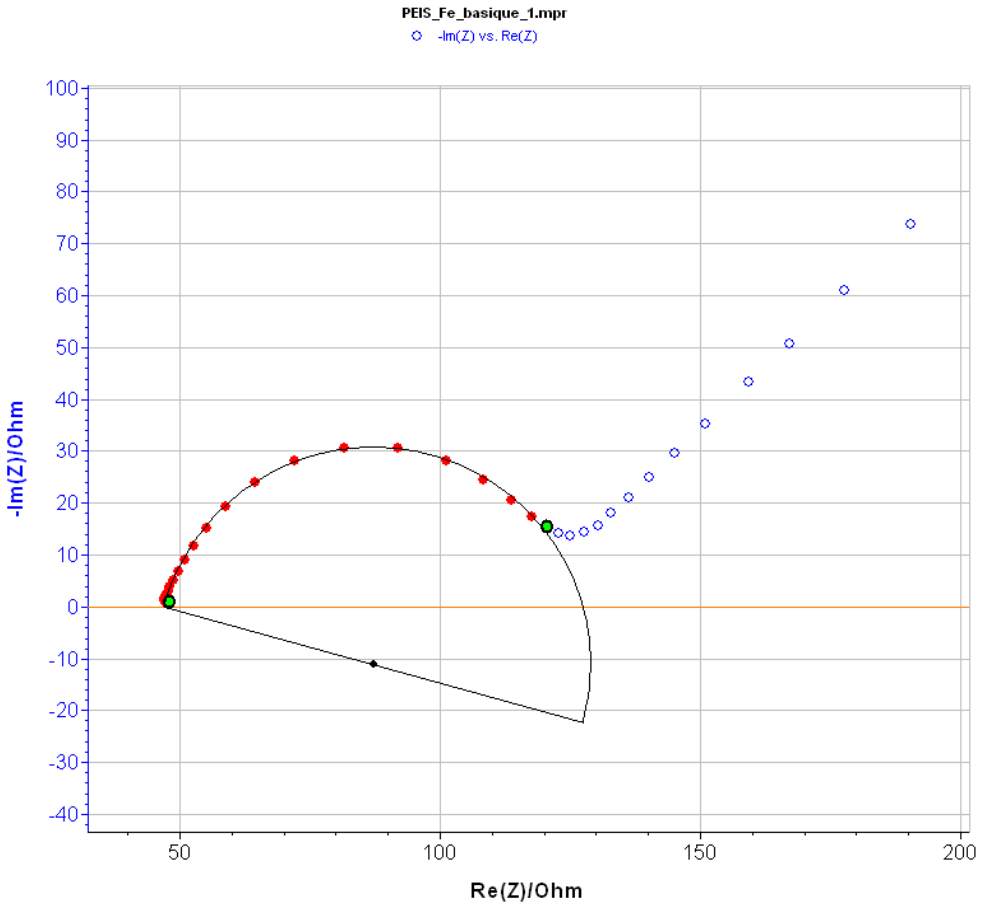


Fig. 111: Circular Fit on the graph.

3.4.1.4 Linear interpolation

An interpolation tool is available with EC-Lab®. The raw data file is not changed after this analysis.

When a data point zone is selected click on "**Calculate**".

The linear interpolation allows the user to space out regularly in time each point of the data file. The user can select to interpolate data by a defined number of points or a regular time between each point. Then a processed interpolated data file is created with the following name: filename_intpl.mpp.

This tool is very useful to subtract two data files. Indeed subtraction between two file is only possible when the files present the same regular distancing between each point.

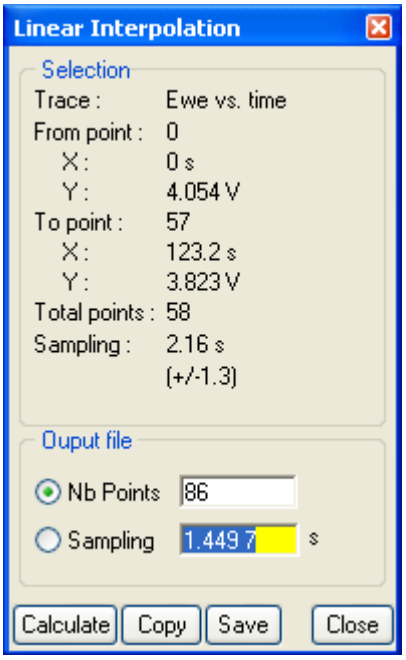


Fig. 112: Linear interpolation window.

3.4.1.5 Subtract files

A tool – for subtracting curves is available with EC-Lab®. The raw data files are not changed after this analysis.
Indeed for some applications, it could be interesting to subtract two curves. The "**Subtract Files**" tool is available in the "**Math**" menu or via the right-click of the mouse.

The two files to subtract are selected as File 1 and File 2. Then, the resulting file (File 1 - File 2) is displayed. The sampling rate of the resulting file in *_filter.mpp format is defined by:

- the sampling rate of file 1 or/and file 2
- the total number of the points of the resulting curve (File 1 – File 2). The spacing can be defined in a linear or logarithmic spacing.
- a constant time step.

The results can be copied in the clipboard to be pasted in the print window comment zone or in a text file. They can be saved in a text file.

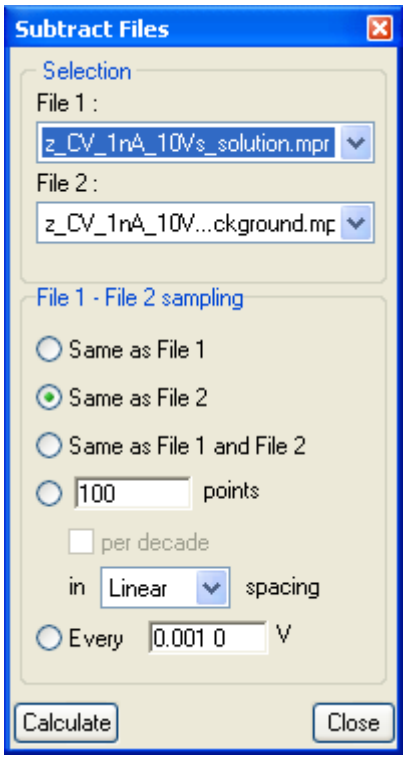


Fig. 113: Linear interpolation window.

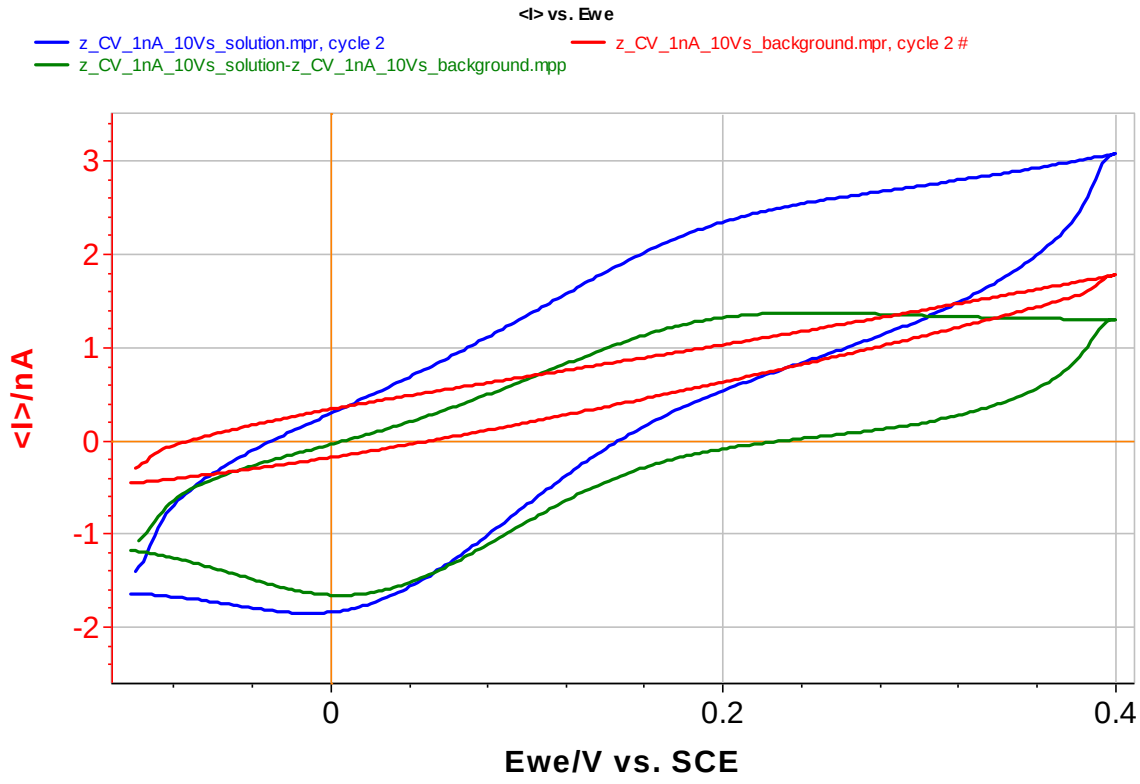


Fig. 114: Use of the Subtract Files tool on the blue and red curves. Obtained curve is given in green.

3.4.1.6 Integral

Much like the Linear Fit method, one can calculate the integral value of a selected trace between two makers.

On the graphic display, select the **Integral** with the Integral button in the analysis menu or the mouse right click and the data points where the fit will be performed. The Integral analysis window is displayed. Click on "**Calculate**". Two markers delimit the integrated trace. The markers can be moved to adjust the fit selected zone. The fit is updated automatically. The integral is calculated according to X-axis. A pinkish area is displayed on the integrated zone.
The units of the integral fit result depend on the plotted data points. For a cyclic voltammetry the units will be A.V.

The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

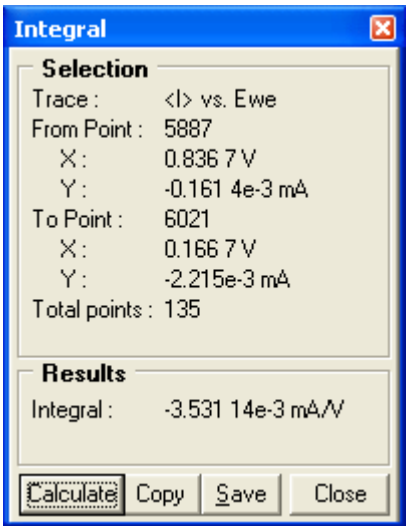


Fig. 115: Integral window.

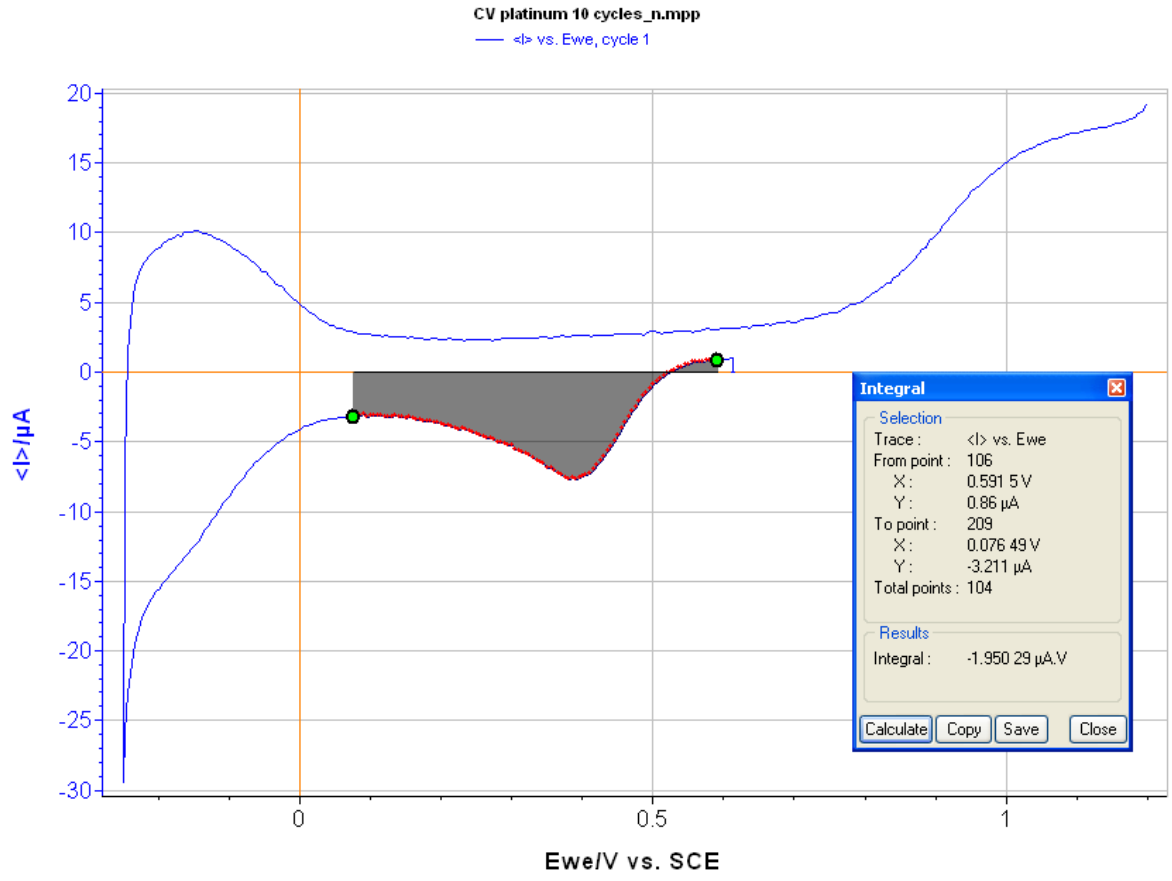


Fig. 116: Integral determination on a trace.

3.4.1.7 Fourier transform

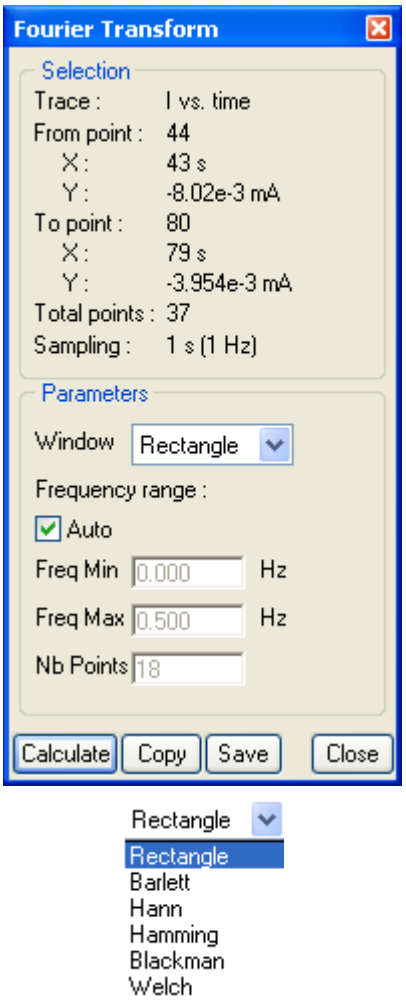


Fig. 117: Fourier Transform window.

This mathematical tool FT{} allows the user to calculate the discrete Fourier transform (DFT), which is a specific kind of Fourier Transform. It transforms one function into another, which is called the frequency domain representation, or simply the DFT, of the original function. But the DFT requires a discrete input function and whose non-zero values have a limited duration.

The calculation is done following the formula:

$$X(f) = \frac{1}{N}\sum_{k=0}^{N-1} x_k \exp(-2i\pi f t_k) \text{ with}$$

$$(x_k)_{k=0\ldots N-1},\ x_k = x(t_k) = x(k\mathrm{d}t)$$

When a data point zone is selected click on "**Calculate**". Once the zone selected, it is possible to choose the shape of the window where the calculation will be done. In signal processing, a window function (also known as an apodization function or tapering function) is a function that is zero-valued outside of some chosen interval. When another function or a signal (data) is multiplied by a window function, the product is also zero-valued outside the interval.

The 6 windows possibilities are described below (relationship only valid within the interval [-1, 1] and 0 outside):

Rectangle: $w(t) = 1$

Barlett: $w(t) = 1 - |t|$

Hann: $w(t) = 0.5 + 0.5\cos(\pi t)$

Hamming: $w(t) = 0.54 + 0.46\cos(\pi t)$

Blackman: $w(t) = 0.42 + 0.5\cos(\pi .5 + 0.08\cos(2\pi t)$

Welch: $w(t) = 1 - \sqrt{t}$

The processed DFT data file is created with the following name: filename_dft.mpp.

This tool is very useful to determine if the measurement is affected by environmental noise, like 50 or 60 Hz.

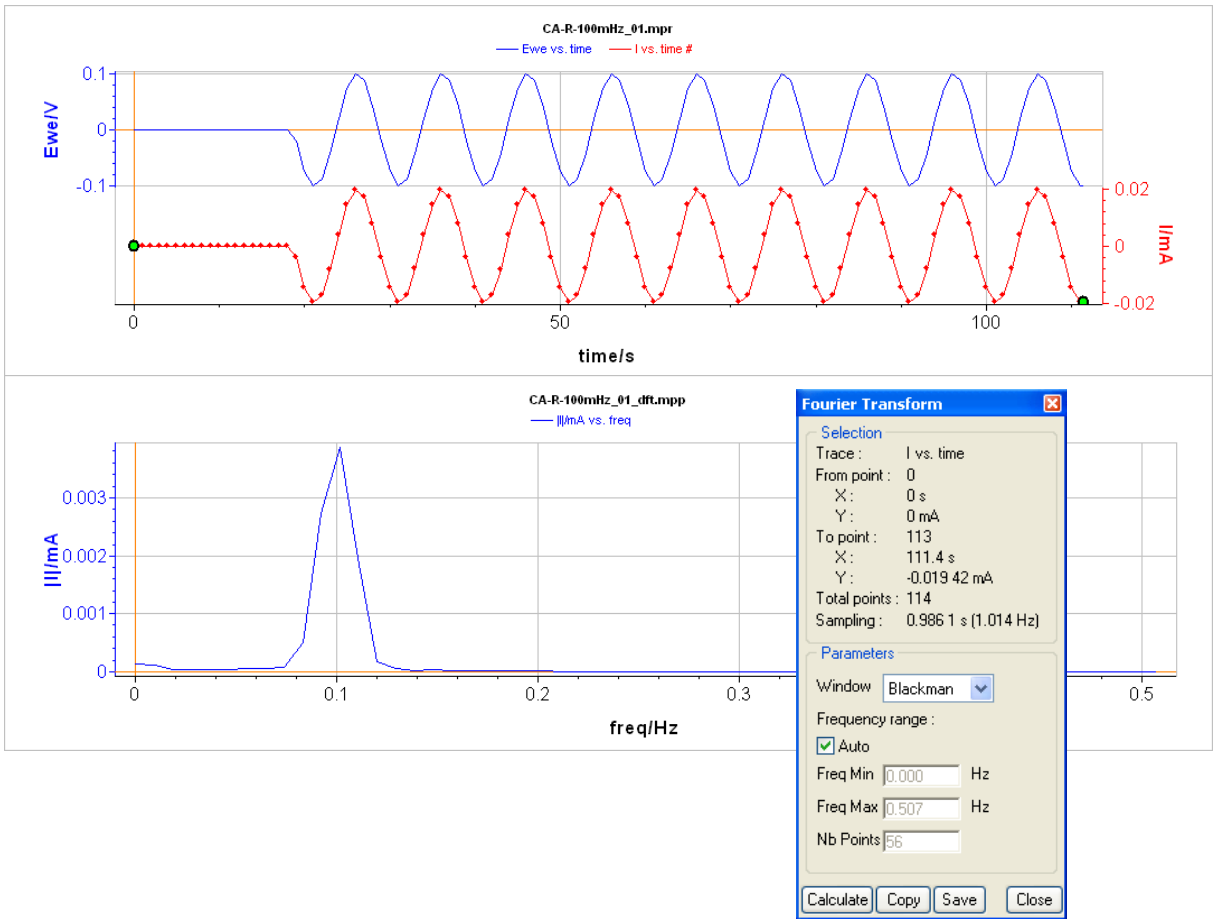


Fig. 118: Fourier transform analysis.

3.4.1.8 Filter

Data may be distorted by external perturbation, for instance the 50 or 60 Hz frequency signal coming from the electrical grid. The "**Filter**" tool available in EC-Lab® software allows the user to remove this additional signal and then yield to smoother results.

Several filtering methods can be set:

- Moving average method. For this method, the window size must be defined.
- Savitzky-Golay method. This method is based on polynomial calculation in a defined window. The window size and the polynomial order have to be set.
- Low/high pass or band pass/reject methods. These methods are based on Fourier Transform. The window (Rectangle, Barlett, Hann, Hamming, Blackman, Welch) and the cutoff frequency(ies) have to be defined (please refer to the Fourier transform part for more details on this point).

The results can be copied in the clipboard to be pasted in the print window comment zone or in a text file. They can be saved in a text file.

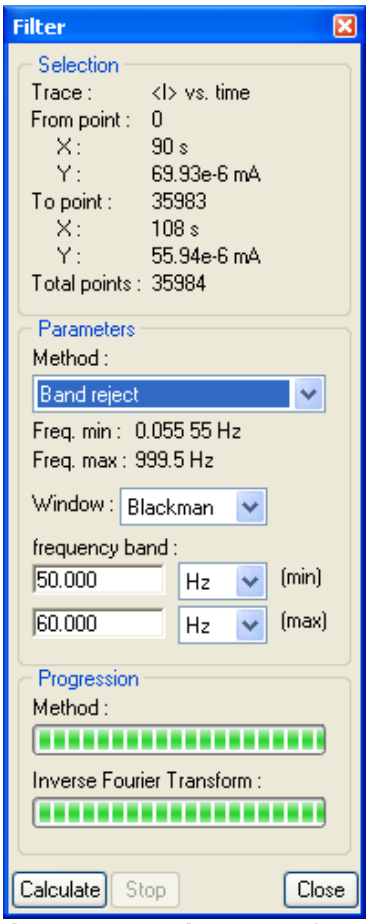


Fig. 119: Fourier Transform window.

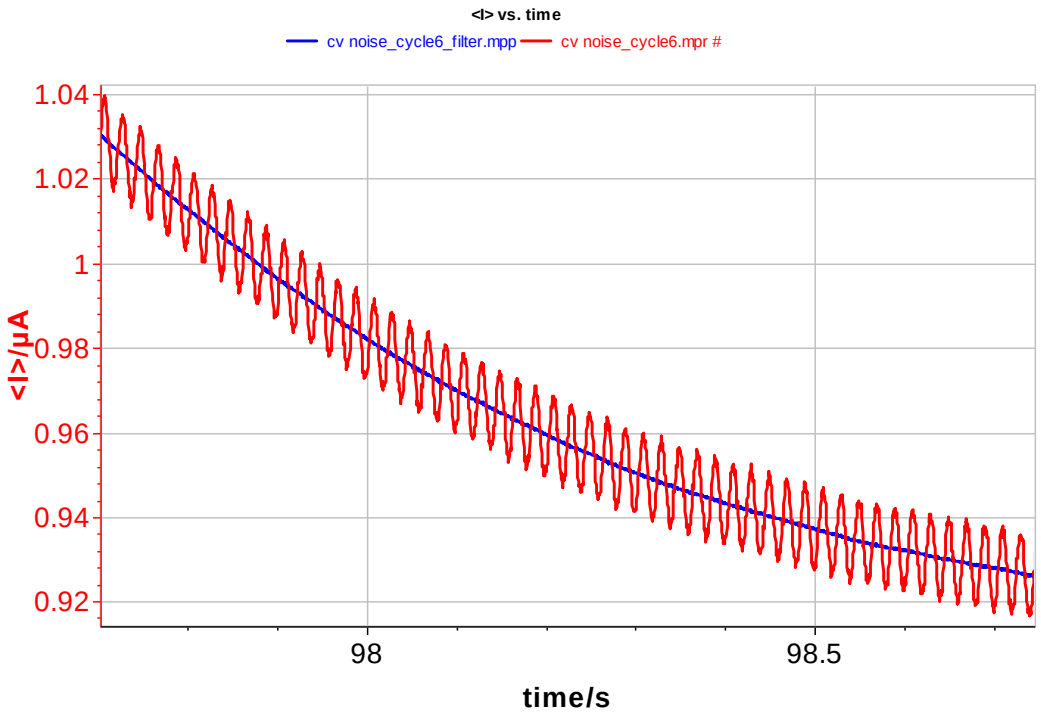


Fig. 120: Filter result. Red curve is the raw data file and blue curve is the filtered curve.

3.4.1.9 Multiexponential Sim/Fit

It is possible to model data with multiexponential behavior (up to order 6) with EC-Lab® software. This tool is particularly interesting for conductivity measurements. A simulation tool "**Multi-Exponential Sim**" and a fitting tool "**Multi-Exponential Fit**" are available in the "**Math"** menu.

Multi-Exponential Sim

This tool allows user to plot a curve from a multi exponential equation. First of all, order of the multiexponential equation is selected (up to 6). Several units for *x*- or *y*-axis can be chosen for the output graph. The window of the simulation is defined between X min and X max. In the third block of the window, it is possible to add noise if the box "Add noise" is ticked. Click on the "**Calculate**" button to obtain simulated curve.

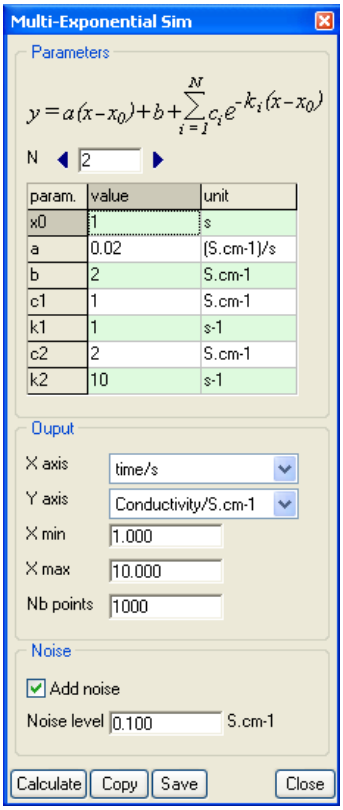


Fig. 121: Multiexponential Sim window.

Multi-Exponential Fit

As previously, the user can select the order of the exponential (up to 6). In the table, a line is created for each parameter. Clicking on "Calculate", the calculation without randomization or fit of the parameters will be done. If the result is not acceptable, it is possible to reach a better fit by clicking on "Minimize". This minimization is only possible when the box associated to the value to minimize is ticked.

The **"Multi-Exponential Fit"** is able to perform a fit on every data displayed in EC-Lab® software. The combo box in the "Fit" block offers two possibilities to initialize the fit from the "Auto estimate" values or from "Current parameters".
Note that the x0 value cannot be fit and must be set manually by the user.

The results can be copied in the clipboard to be pasted in the print window comment zone or in a text file. They can be saved in a text file.

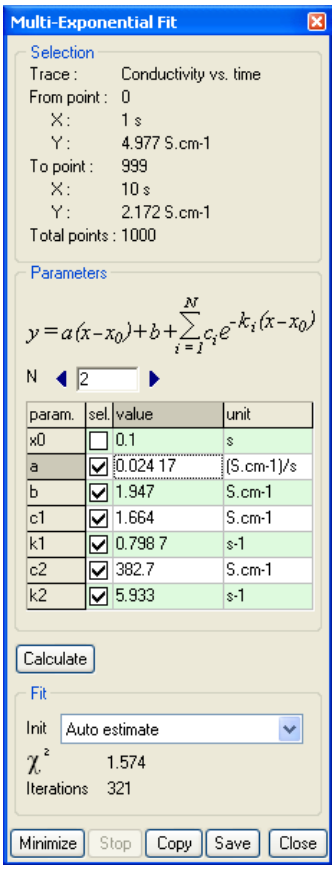


Fig. 122: Multiexponential Fit window.

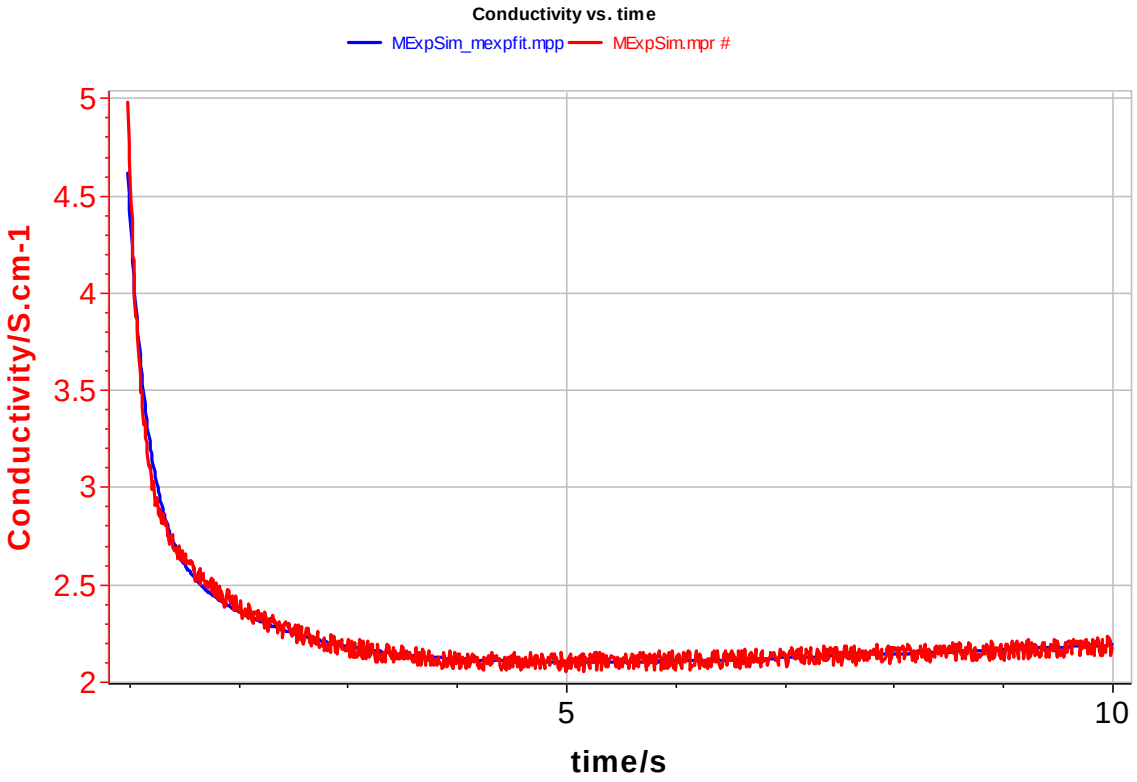


Fig. 123: MultiExponential fit result.

3.4.2 General Electrochemistry Menu

3.4.2.1 Peak Analysis

A peak analysis is available with the EC-Lab® software. Like other analyses with the EC-Lab® software, the user has to select the analysis and then select the data points to fit or select the data points before choosing the fit. To select the peak analysis click on the button in the graphic tool bar or select peak analysis in the right click analysis menu. When this first part is done, the peak analysis consists of two steps. First the user must choose the baseline and second click on calculate to have the results.

3.4.2.1.1 Baseline selection

When selected the peak analysis window is displayed with two tabs **Baseline** and **Peak**. In the Baseline tab the user must select the baseline type. Three selections are available, no baseline, linear baseline and polynomial baseline.

If the user selects **NO** the analysis will be performed according to the abscissa axis. If the user select **LINEAR** three different baselines can be set in **manual** mode (with markers locked on the curve) or **regression** mode (with a linear regression made on the capacitive part of the curve before the peak) or in a **free** mode (two cursors defining a straight line unlocked to the curve).
If the user selects **Polynomial** a polynomial baseline is plotted and adjusted to the data points in the following way: two data zones are used for the polynomial fit at the beginning and at the end of the selected zone (twenty first points and twenty last points of the selected data zone). The selected data zone and the polynomial fit are limited by two cursors that can be adjusted for a better fit. The polynomial fit used is defined as follows: $y = ax^3 + bx^2 + cx + d$. The results of the fit are automatically calculated when a cursor is moved.

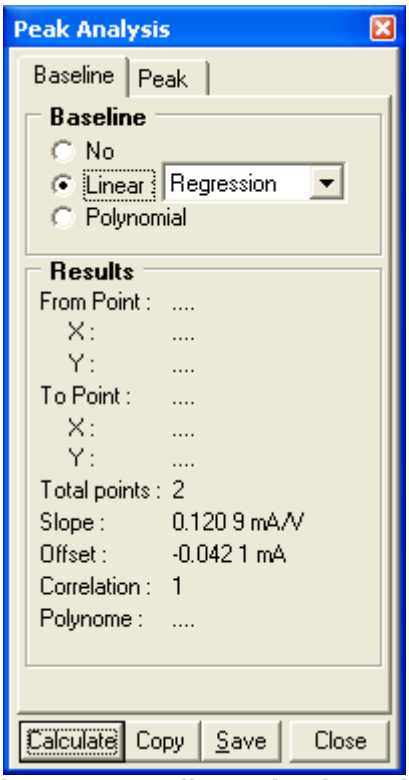


Fig. 124: Baseline selection tab.

In the manual mode the baseline is defined by two points represented by circles and set on the curve at the extremities of the zone of selected points.

In the regression mode, the regression straight line determination is made with the least square method. Data points used for the regression are automatically selected in the first 25 percents of the total point number between the beginning of the selected zone and the point corresponding to the max current value.
The results frame displays the baseline equation and the data point zone used for the regression.

3.4.2.1.2 Peak analysis results

When the baseline type is selected click on **Calculate.** The software will automatically find the max current value in the selected zone according to the baseline.
Data points used in the peak analysis are selected by default from 35 % of the beginning of a zone (starting at the beginning of the selected zone and ending at the max current value), to the end of the zone. The data point zone for the analysis is shown in the **Selection** frame by the extreme points.

The results of the analysis are displayed in the **Results** frame. Several values for the peak are displayed: the position (E_p), height, width (1/2), E_p - $E_{p/2}$, charge pos. and charge neg. These values are explained below.
The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

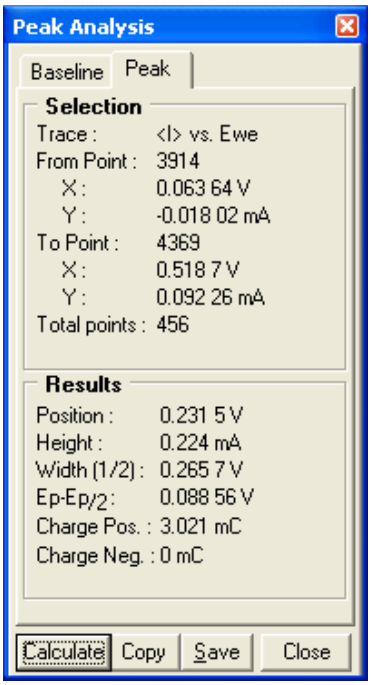


Fig. 125: Peak results tab.

3.4.2.1.3 Results of the peak analysis using a linear regression baseline

The following figure shows the result of the peak analysis performed on a cyclic voltammetry data file. The baseline used for the analysis is a linear regression baseline.

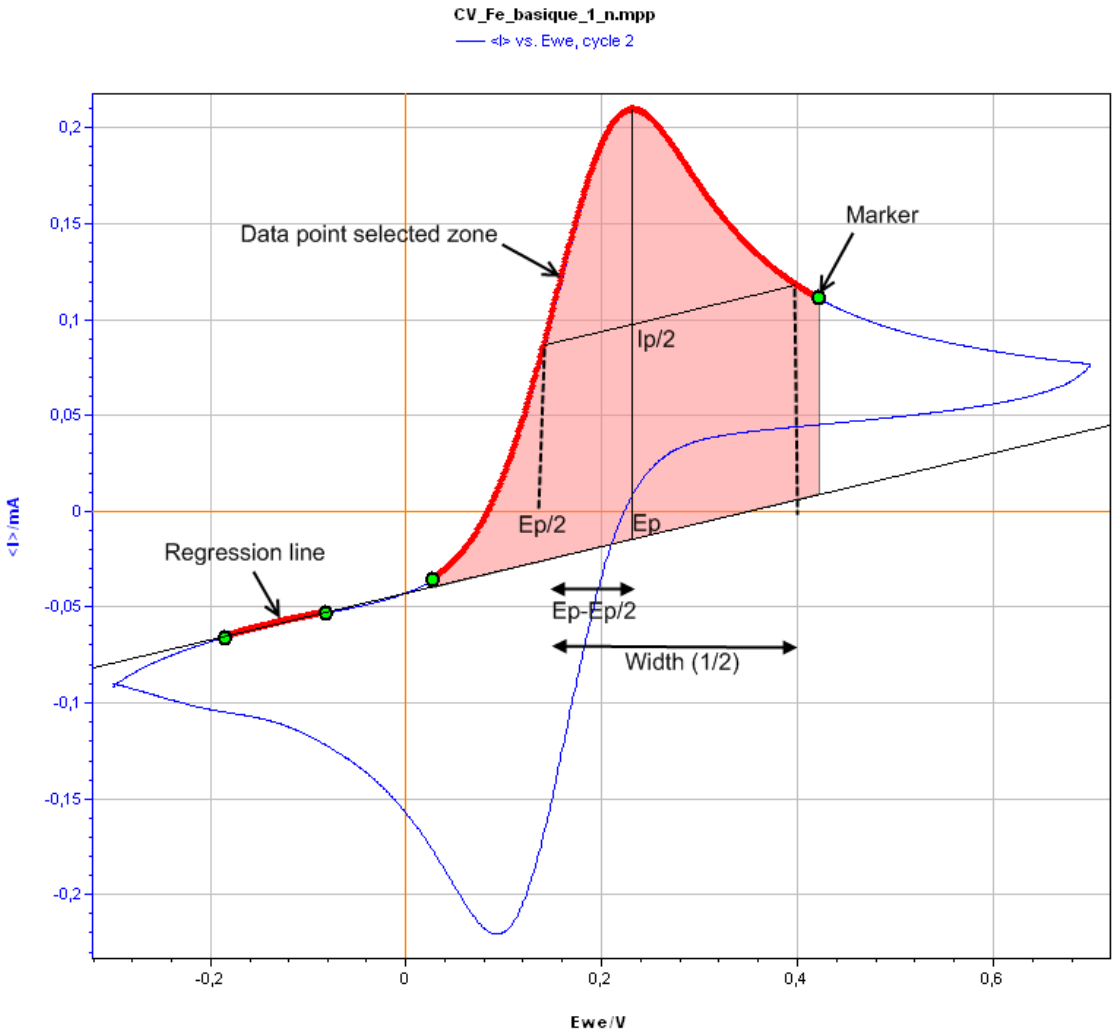


Fig. 126: Oxidation peak analysis on a cyclic voltammetry experiment using a linear regression baseline.

The different values in the result frame of the peak analysis window are as follows:

- **Position** is the potential (E_p) corresponding to the max current value (determined according to the baseline).
- **Height** is the current value for the potential E_p (always according to the baseline).
- **Width (1/2)** is the potential peak width determined (when it is possible) at half the peak height (parallel to the baseline).
- **E_p-$E_{p/2}$** is the semi-width for the growing part of the peak.
- **Charge Pos.** is the charge corresponding to the integration of the peak versus time according to and above the baseline (in the case of an oxidation peak). The part of the peak considered for the calculation of the charge is limited to the green circle markers. This zone can be adjusted by moving the markers.
- **Charge Neg.** is the complementary part of the charge in the case where the selected zone crosses the baseline (below the baseline for an oxidation peak).

Note: it is possible to save the results of the analysis to a text file using the copy option. The results are copied to the clipboard and can be pasted in notepad or other software.

3.4.2.1.4 Results of the peak analysis using a polynomial baseline

In fact, it is often difficult to apply a linear regression to simulate the capacitive part of a curve or remove the beginning increasing part of a second current peak. A polynomial baseline could lead to a more significant fit. On the following figure a polynomial baseline has been used to do a peak analysis. The oxidative peak of a polypyrrol film is analyzed using a polynomial baseline. With this baseline, we can avoid taking into account the beginning part of the pyrrol monomer oxidation. The result variables are the same as for the analysis with a straight baseline.

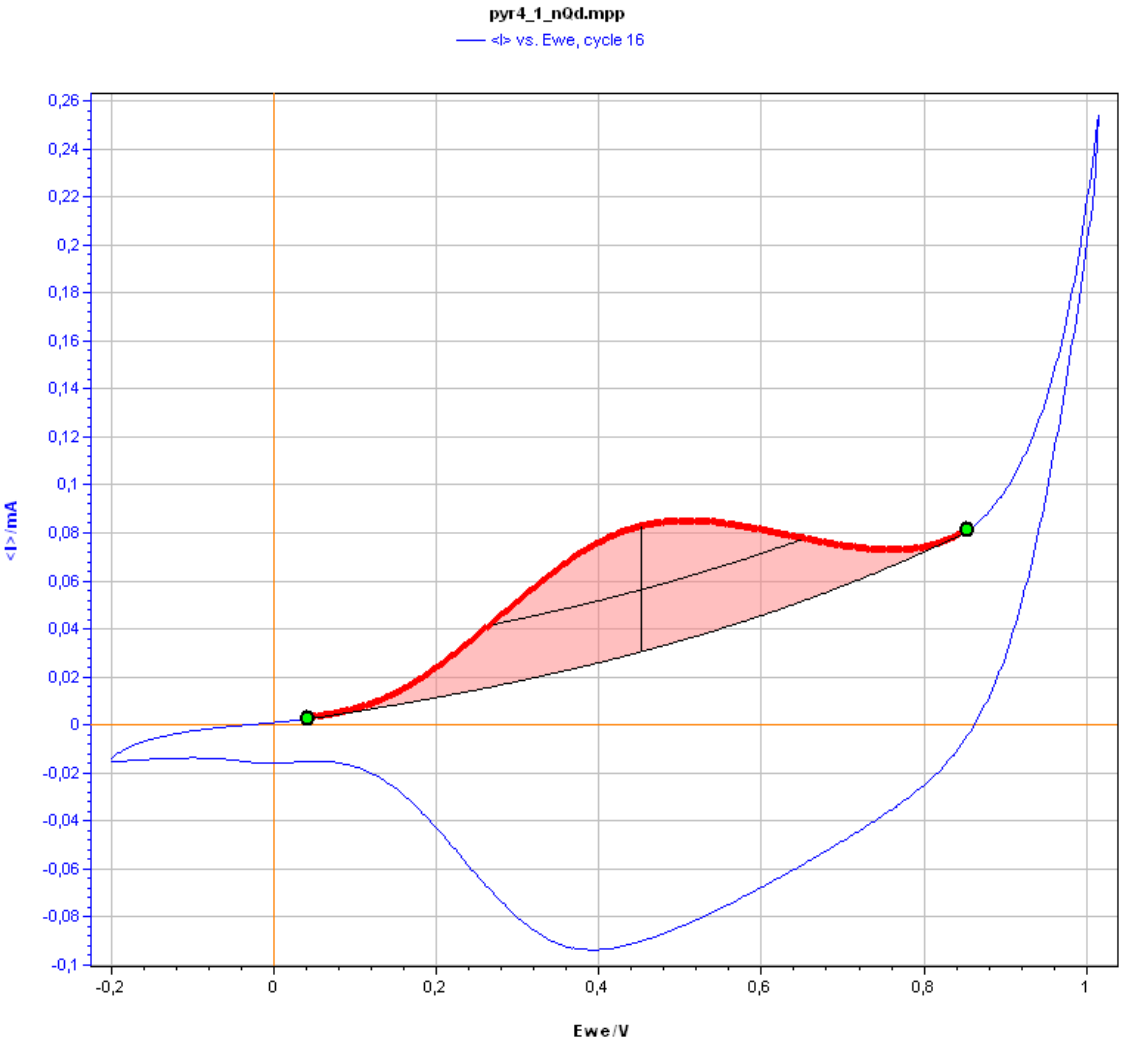


Fig. 127: Peak analysis on a cyclic voltammetry experiment using a polynomial baseline.

3.4.2.2 Wave analysis

The wave analysis is the most useful tool for the analysis of experiments performed in a hydrodynamic regime (specially a rotating disk electrode).

When a data point zone is selected click on "**Calculate**".
The wave analysis is made according to two straight lines. These lines are defined using a linear regression fit. The software will automatically find the two parts of the curve with the weakest slope for the fit. For the first regression the first 20 % of the selected data points are taken into account. The last 20 % of the selected data points are taken into account for the second regression.
The data point zone for the analysis is shown in the **Selection** frame by the extreme points.

The Results of the analysis are displayed in the **Results** frame. Several values for the wave are displayed: $E_{1/2}$ and the limit anodic and cathodic currents.

The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

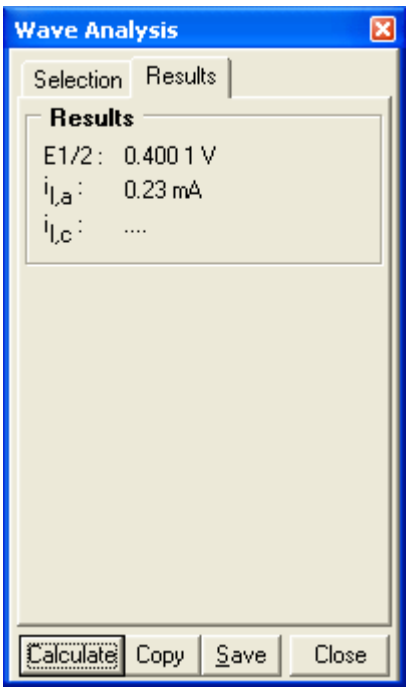


Fig. 128: wave results tab.

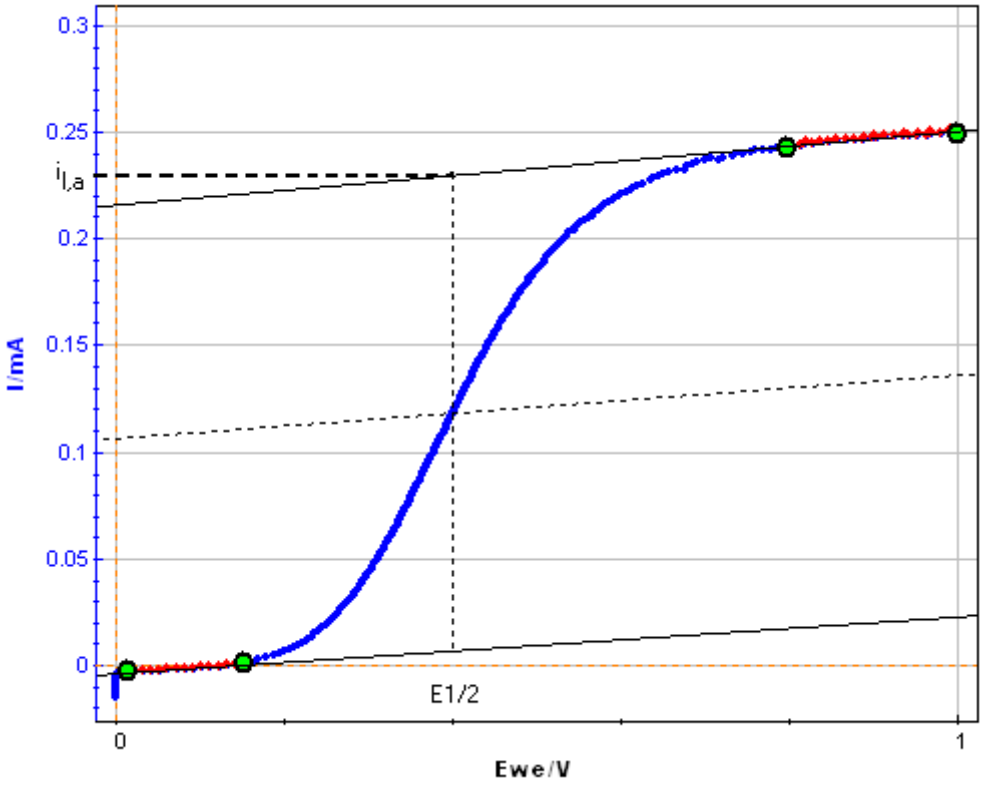


Fig. 129: Wave analysis on a curve resulting from a RDE experiment.

$E_{1/2}$ is the half-wave potential obtained by the intersection of the curve with the median between both linear regressions. $I_{l,a}$ is defined by the current value for $E = E_{1/2}$ on the top linear regression(for the oxidation reaction).

3.4.2.3 CV sim

CV Sim is a tool designed for the simulation of cyclic voltammetry curves. It is a useful tool to elucidate the mechanism of an electrochemical reaction.

To perform the simulation, it is assumed that:

- Only one species (Red or Ox) is initially in the solution
- The Initial current is equal to zero. So the voltage sweep will start from the open circuit voltage.

First to perform the simulation, the user has to define the number of electron transfer steps that are involved in the mechanisms *via* the combo box. E represents a mechanism with one electron transfer (E); and so on up to 5 electron transfer (EEEEE). Depending on the number of electron transfers selected the corresponding number of tabs appears.

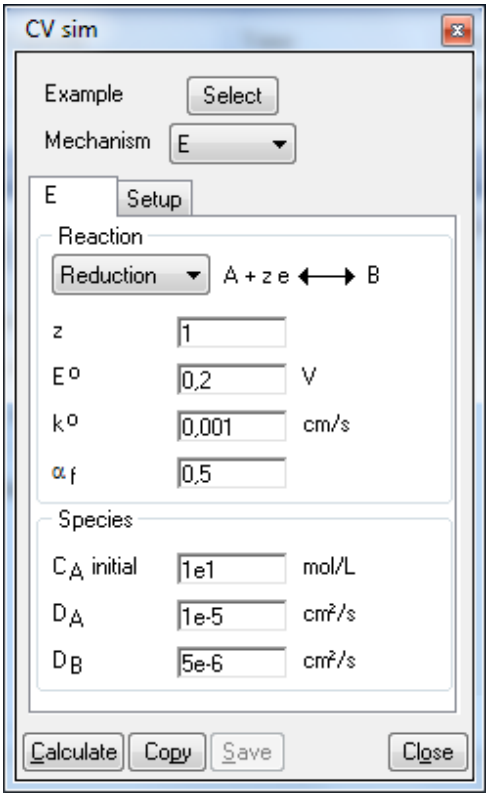


Fig. 130: CVSim window with a single transfer.

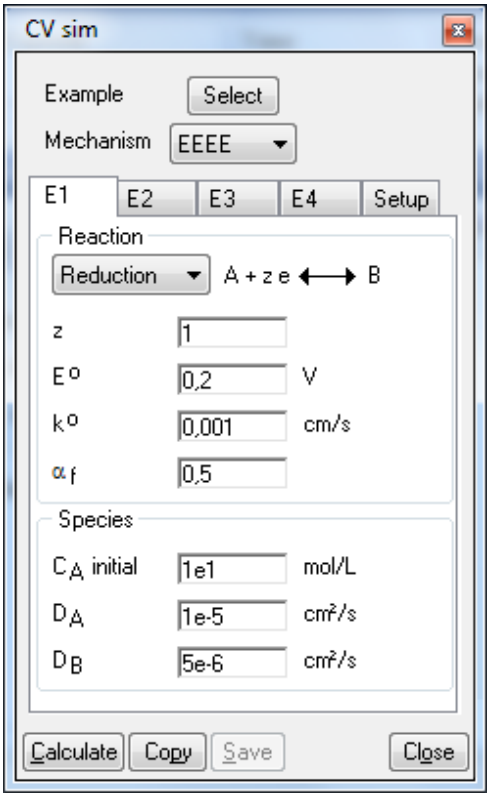


Fig. 131: CVSim window with several transfers.

For each step, the type of reaction and the species characteristics are set in two different frames:

1. Reaction:
   - Reduction or oxidation has to selected by the combo box
   - z represents the number of electron involved in the electron transfer
   - E° is the standard potential of the electron transfer step

- k° is the heterogeneous rate constant
– α_f is the charge transfer coefficient in the forward direction

2. Species:
- Cx is the concentration of the specie x. As it is assumed that only one specie is initially in the solution, concentration is only set in the first step of the mechanism.
- Dx are the diffusion coefficients of the species x.

The experimental conditions are set in the "**Setup**" tab which is divided in five blocks:

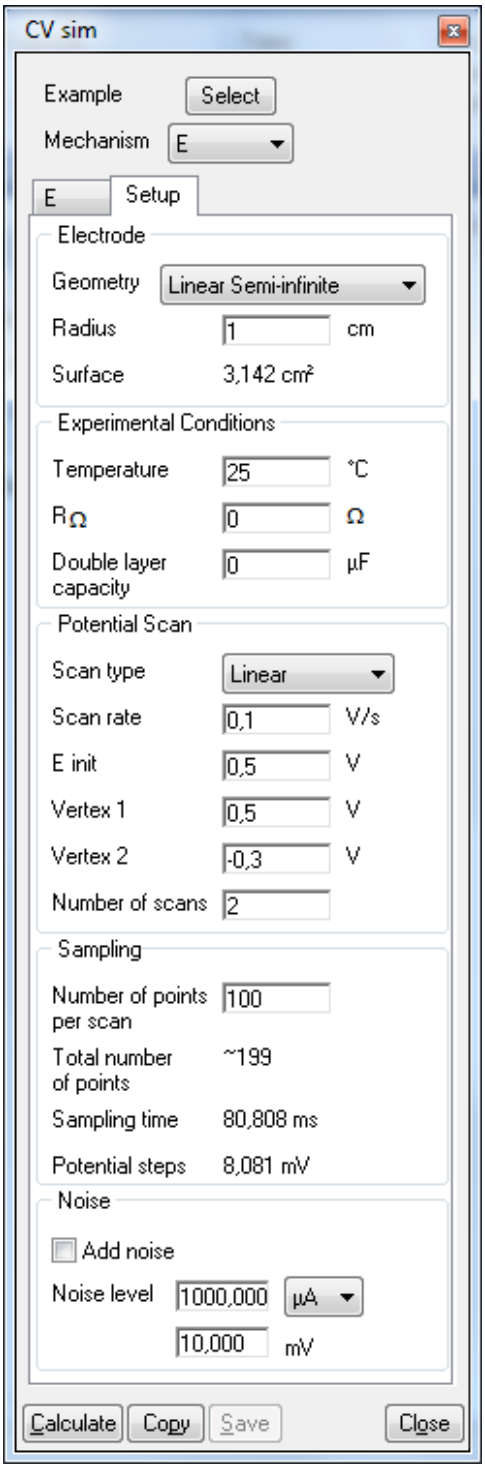


Fig. 132 : "Setup" tab of CVsim

- Electrode:

- Geometry of the electrode can be linear semi-infinite or spherical semi-infinite
- The surface area of the electrode is calculated from the value of the radius of the electrode

- Experimental conditions

- Temperature in degree Celsius
- R_Ω: the resistance in Ohm
- Double layer capacity in µF

- Potential scan

- Scan type: linear or sinusoidal scan, respectively for CV or LASV simulation
- Scan rate in V per second
- The initial and the two vertex potential in V
- Number of scans performed for the CV or LASV simulation

- Sampling

- The user defines the number of points needed per scan to perform the simulation. The total number of points, the resolution in time and in voltage is indicated.

- Noise

- Some noise in current or in voltage can be superimposed to the simulated curve.

When all the parameters are set, the user has to click on the calculate button to display by default the simulated CV curve.

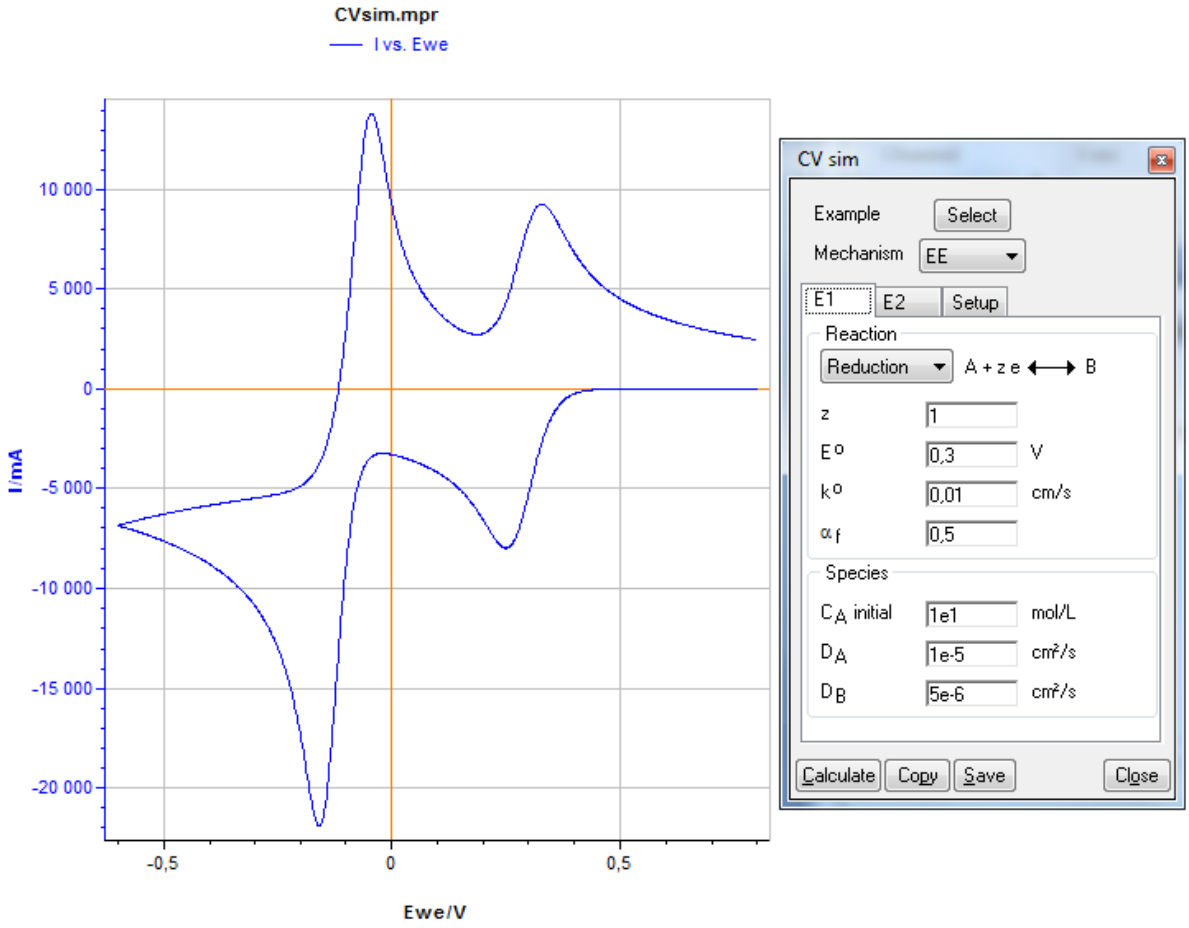


Fig. 133: CV simulation with two electron transfer.

It is also possible to display the interfacial concentration of the electroactive species involved in the mechanism. The resulting curve can be saved as mpr file.

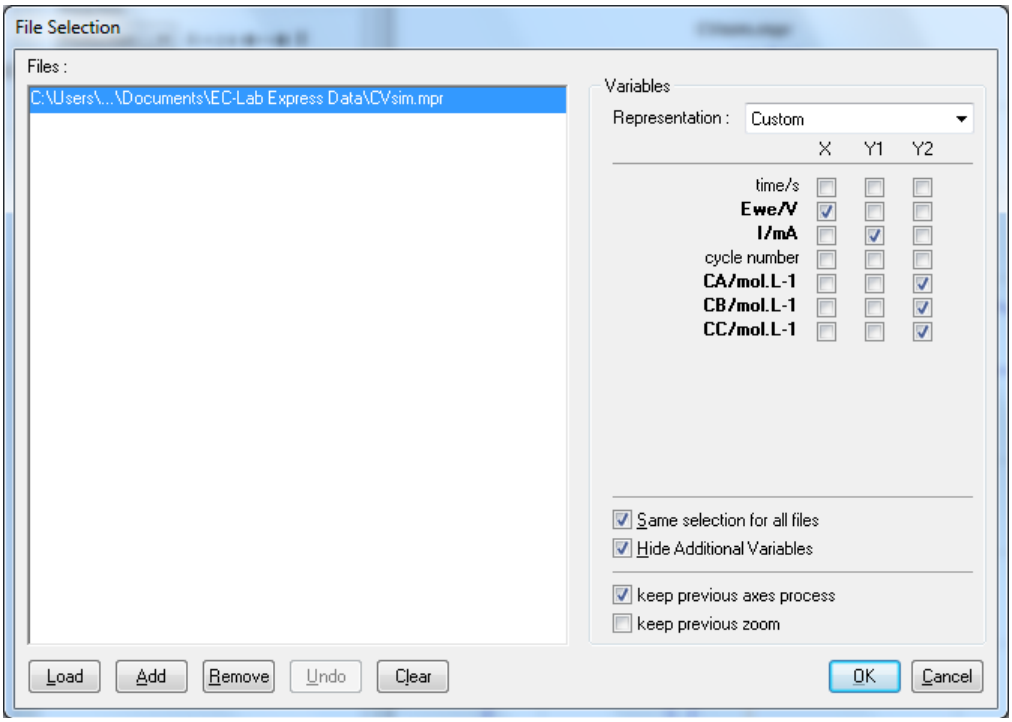


Fig. 134: Variable selection window to display concentrations.

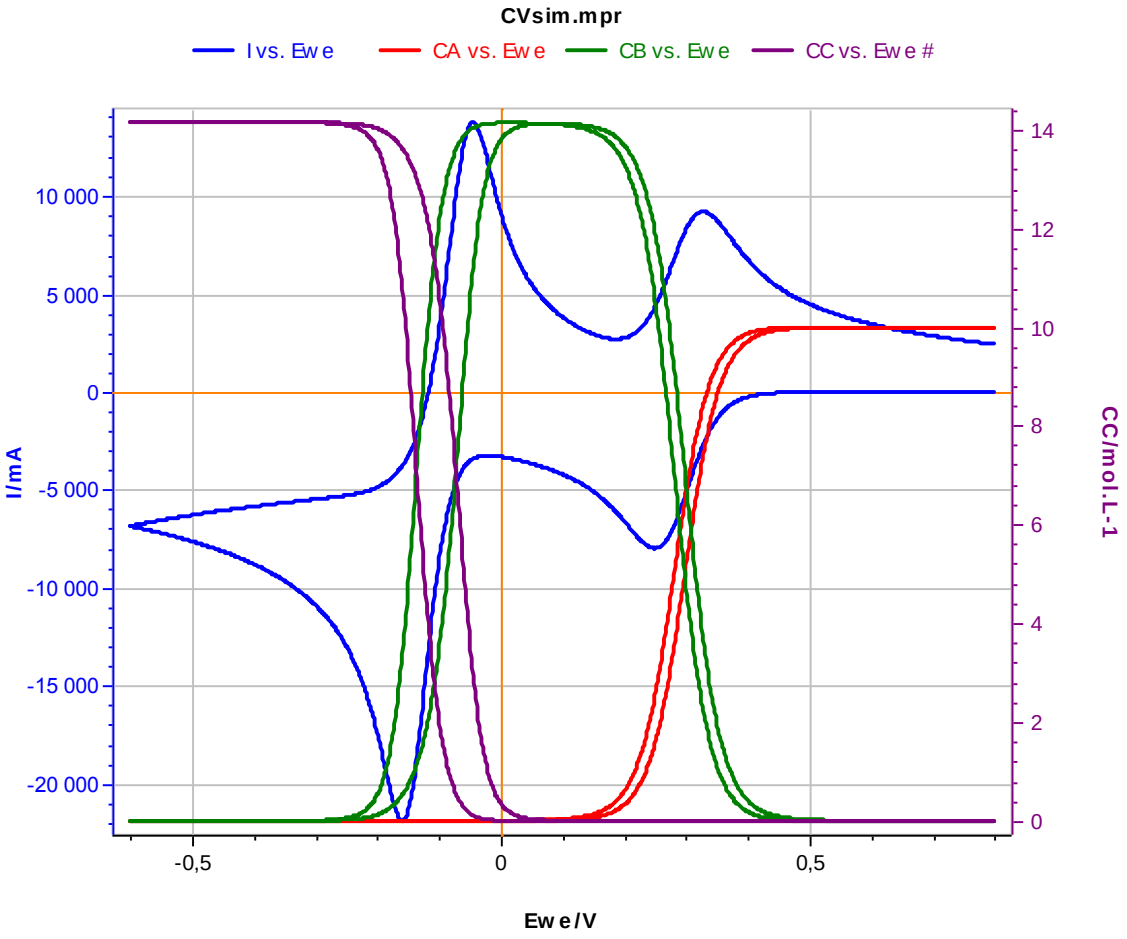


Fig. 135: Interfacial concentration variation versus electrode potential.

Several examples are available in the **CVsim** window. To display an example, one has to click on the “select” button on the top of the “**CVsim**” menu. Then **CVsim** examples window appears to select the mechanism of interest:

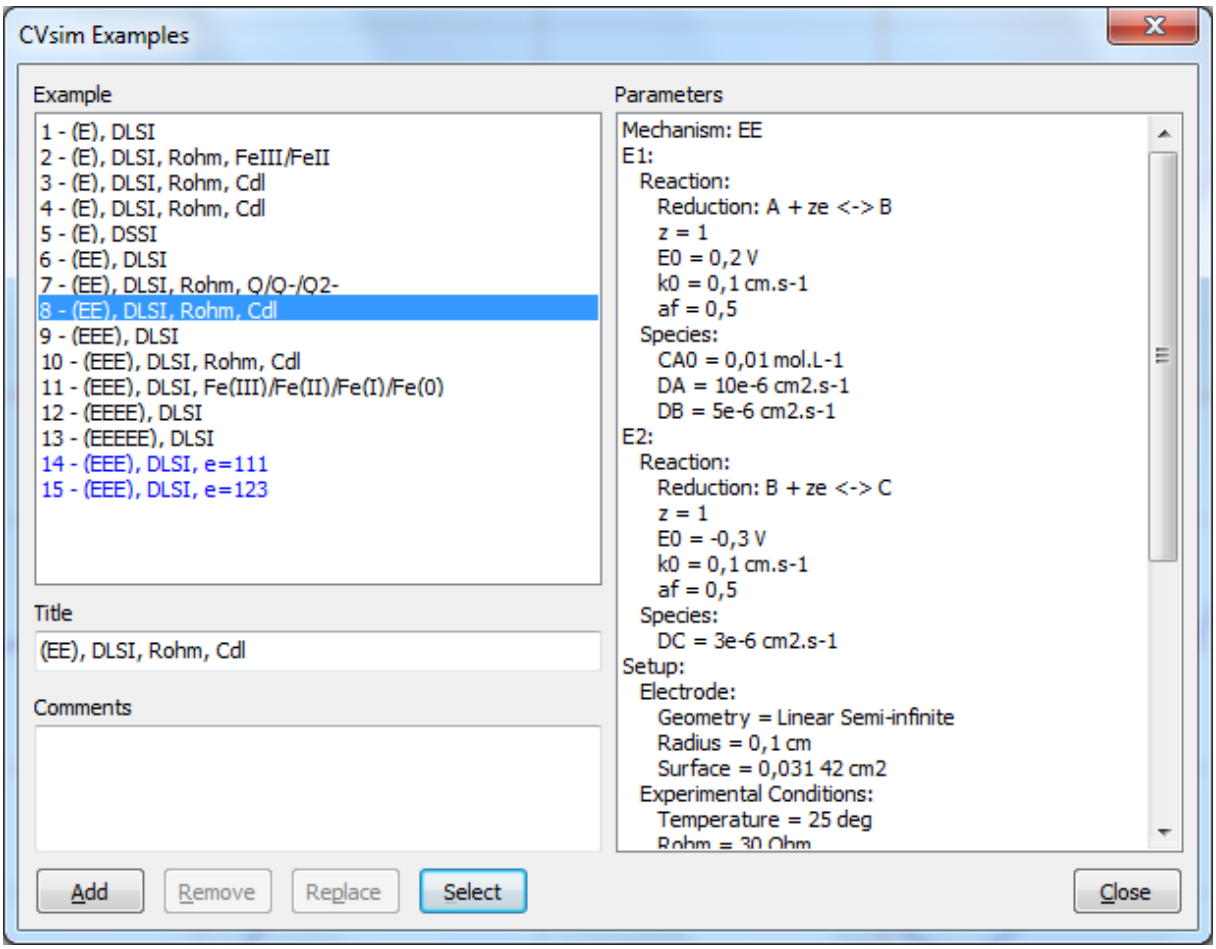


Fig. 136: CVsim examples window.

15 examples are available in this window. The corresponding parameters are displayed on the right column. When clicking the “Add” button, the corresponding curve is displayed.

3.4.3 Electrochemical impedance Spectroscopy menu

3.4.3.1 Impedance data analysis: Simulation, Fit and Kramers-Kronig criterion

Impedance analysis is a powerful tool to determine the kinetic of an electrochemical reaction and values of the kinetic parameters. Electrochemical impedance data analysis allows the user to propose an electrochemical reaction mechanism. To be interpreted, electrochemical impedance data points need a comparison with an electrical circuit simulating the electron and electroactive species at the electrode surface/solution interface. Indeed, this process is assumed to be represented by an equivalent circuit of resistors, capacitors, inductors and diffusion elements. The total current is, in most cases, the sum of distinct contributions from the faradic process and double layer charging.

3.4.3.1.1 Electric equivalent elements: description

The impedance analysis tool contains currently 8 different electric components. These components are:

- R: resistor,
- L: self/inductor,
- C: capacitor,
- Q: constant Phase Element (CPE),
- W: Warburg Element simulating the semi-infinite diffusion,
- Wd: Warburg Diffusion Element simulating the convective diffusion,
- M: restricted Linear Diffusion Element,
- G: Gerischer Element.

3.4.3.1.2 Resistor: R

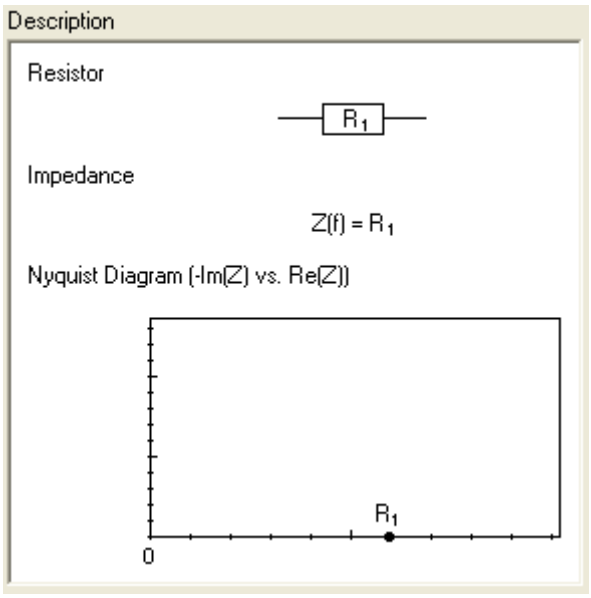


Fig. 137: Resistor element description.

The resistor element is defined as a passive component with a constant value when frequency varies. Fig. 137 describes the resistor with its symbol, its faradic impedance and a view of its Nyquist representation. The resistor element is characterized by a constant value that can be measured in the Nyquist diagram by the Real part ($\mathrm{Re}(Z)$) for an imaginary part to zero ($-\mathrm{Im}(Z)=0$).

3.4.3.1.3 Inductor: L

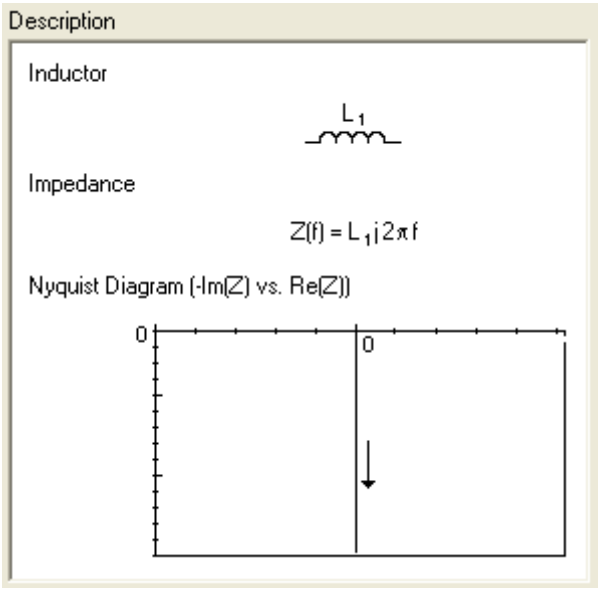


Fig. 138: Inductor element description.

The inductive element has impedance with a frequency dependency (as shown on the faradic impedance equation). The Nyquist plot of an inductance is a vertical straight line in the imaginary negative part ($-\mathrm{Im}(Z) < 0$).

3.4.3.1.4 Capacitor: C

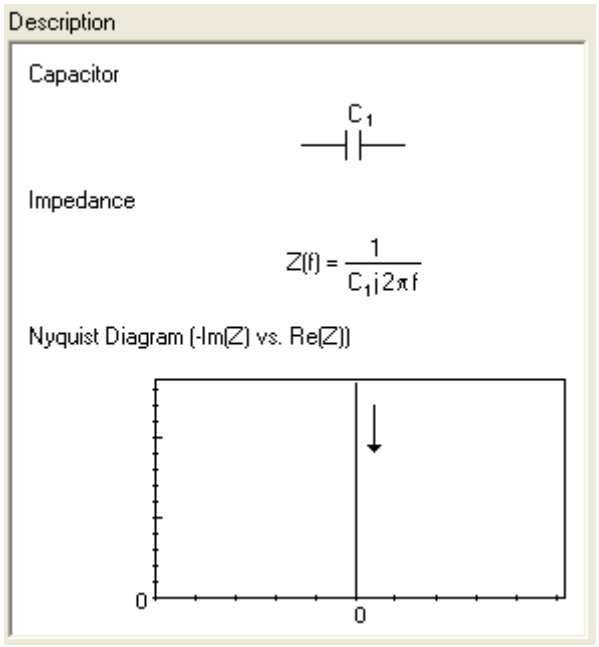


Fig. 139: Capacitor element description.

The capacitor impedance is also frequency dependent. The Nyquist plot of such an element corresponds to a vertical straight line in the imaginary positive part (-Im(Z)>0). The faradic impedance decreases when the frequency increases.

3.4.3.1.5 Constant phase element: Q

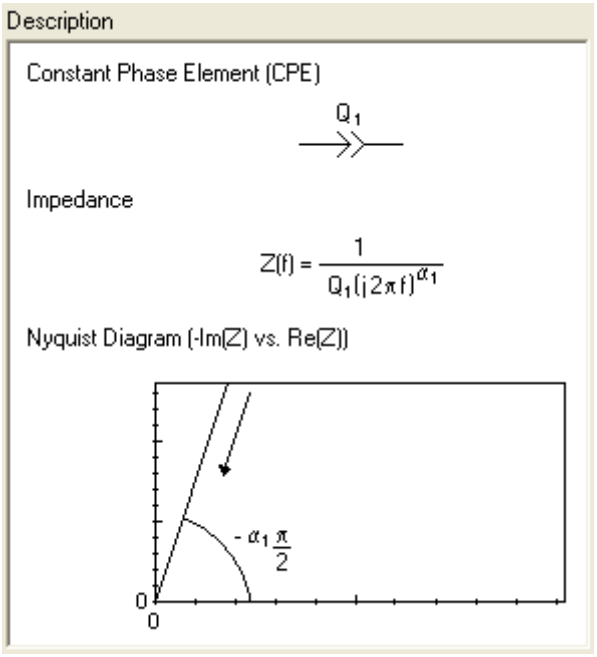


Fig. 140: Constant Phase Element description.

The CPE impedance is also frequency dependent. The Nyquist plot of such an element corresponds to a straight line in the imaginary positive part (-Im(Z)>0) with a $-\alpha\pi/2$ angle with the real axis. The faradic impedance of the CPE decreases when the frequency increases.

3.4.3.1.6 Warburg element for semi-infinite diffusion: W

The Warburg element can be used to simulate a semi-infinite linear diffusion that is unrestricted diffusion to a large planar electrode.

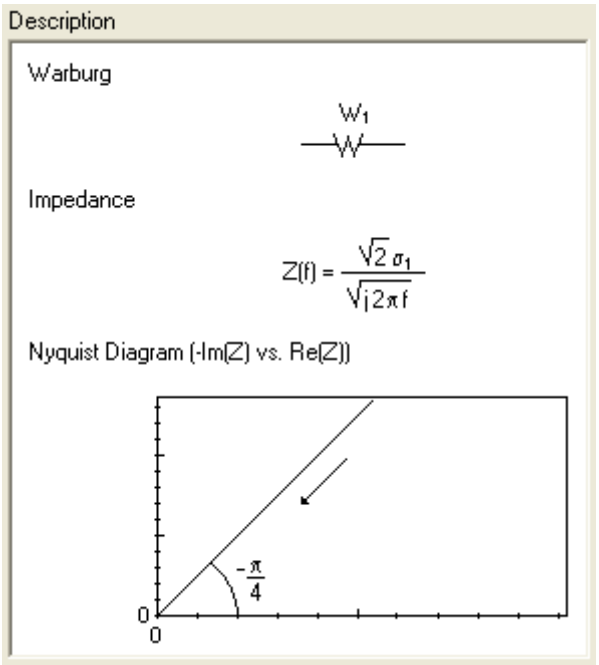


Fig. 141: Warburg diffusion element description.

The Warburg impedance is an example of a constant phase element for which the phase angle is constant $-\pi/4$ and independent of frequency. The Warburg is unique because absolute values of the real and imaginary components are equal at all frequencies.

3.4.3.1.7 Warburg element for convective diffusion: W_d

The Warburg element for a convective diffusion is an approximation mainly used in case of diffusion on a Rotating Disk Electrode in a finite length. The mass transport is supposed to happen only by diffusion in the Nernst diffusion layer and the solution is considered homogeneous outside this layer. The impedance when the material diffuses through the Nernst Diffusion Layer is described by W_d.

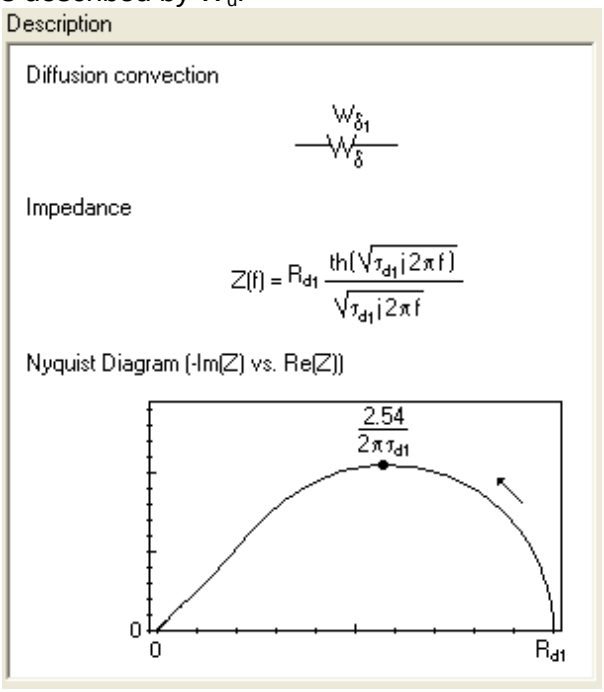


Fig. 142: Warburg element for convective diffusion.

The Warburg element for convective diffusion is equivalent to the Warburg element in the high frequency range ($f \rangle\rangle \frac{2.54}{2\pi\tau_{d_1}}$).

3.4.3.1.8 Linear diffusion element: M

This diffusion element is used for finite length linear diffusion, for example in the case of insertion reactions.

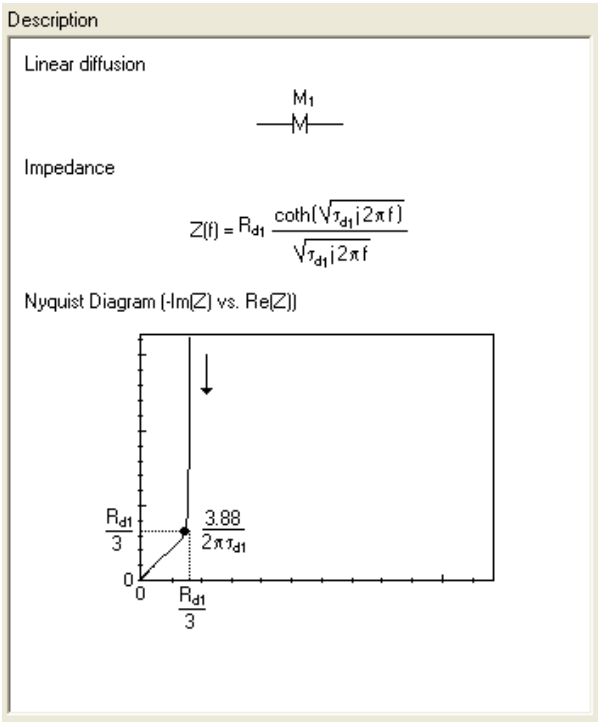


Fig. 143: Linear Diffusion element.

The linear diffusion element is equivalent to the Warburg element in the high frequency range $f \rangle\rangle \frac{3.88}{2\pi\tau_{d_1}}$ and to an R and C in series circuit in the low frequency range.

3.4.3.1.9 Gerischer element: G

The Gerischer circuit element arises when an electroactive species undergoes a chemical reaction in the bulk.

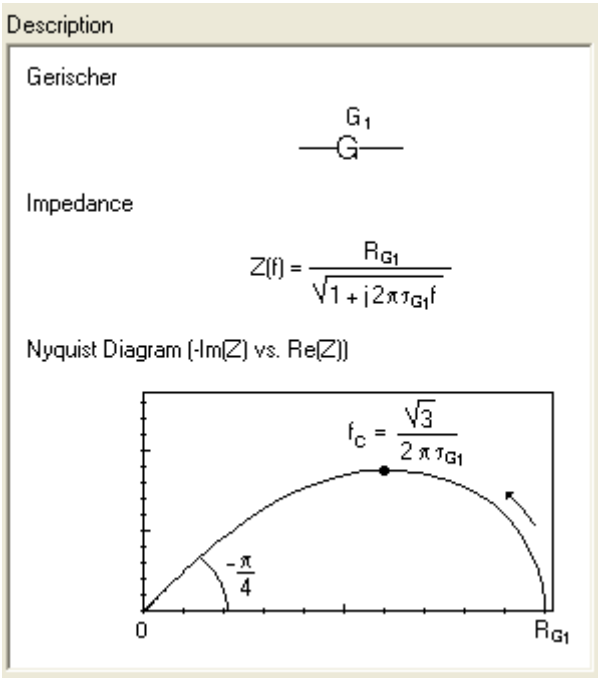


Fig. 144: Gerischer Diffusion element.

Note: This list can be continued by new electric elements whenever our customers define a significant one.

3.4.3.2 Simulation: ZSim

In order to define the equivalent circuit after an impedance experiment, the user can create an electrical circuit and plot the corresponding Nyquist impedance diagram in a given frequency range. To illustrate the capabilities of this tool, let's consider the ZPOT_Fe_basique.mpr data file that the user can find in the sample folder (c:\ECLab\data\sample). The aim of this section is to define the appropriate circuit for the fit.

The data file that will be used in the simulation section and the fitting section has been made from an iron solution on a gold disc-working electrode in a pure diffusion regime in the potentio mode at the open circuit potential. Open the "**ZPOT_Fe_basique.mpr**" data file in the "**File**" menu ("**Load data file…**"). The following window will be displayed:

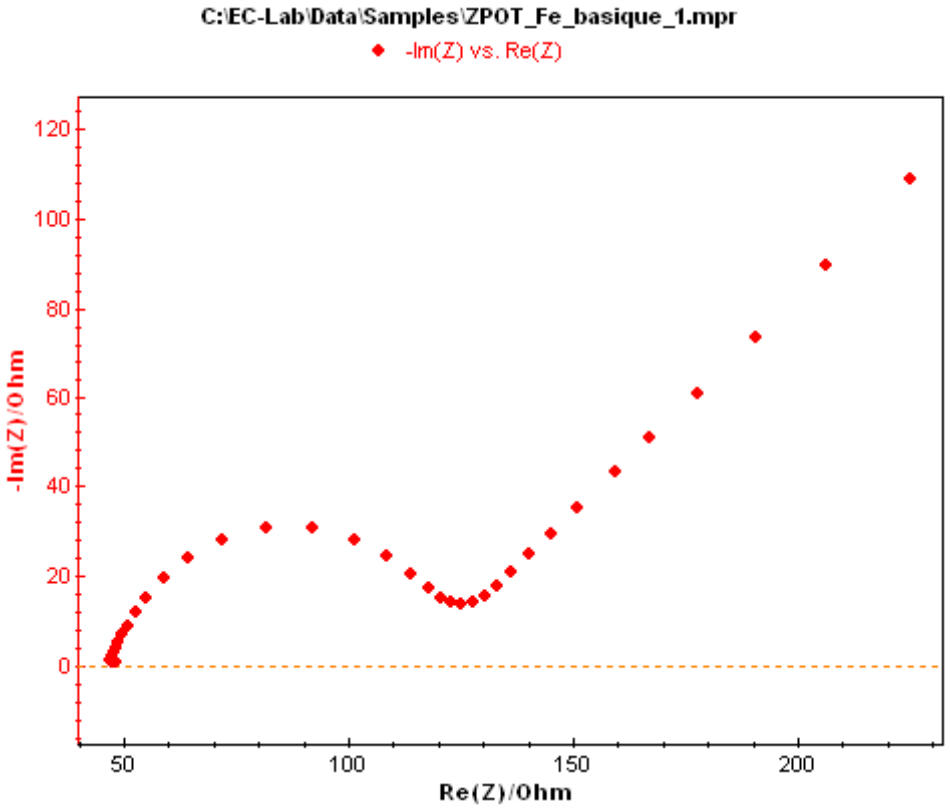


Fig. 145: Experimental Nyquist impedance data file.

This is a typical impedance data file performed in a pure diffusion regime in a solution containing both Ox and Red species of a redox system.

3.4.3.2.1 ZSim window

1st step:

To simulate a curve with the same shape as the previous experimental results, click on ZSim icon or right click on the graph and select "**Analysis/ZSim**". Then the ZSim selection window appears with the corresponding graphic window. This window shows the simulated graph of the circuit with the values selected.

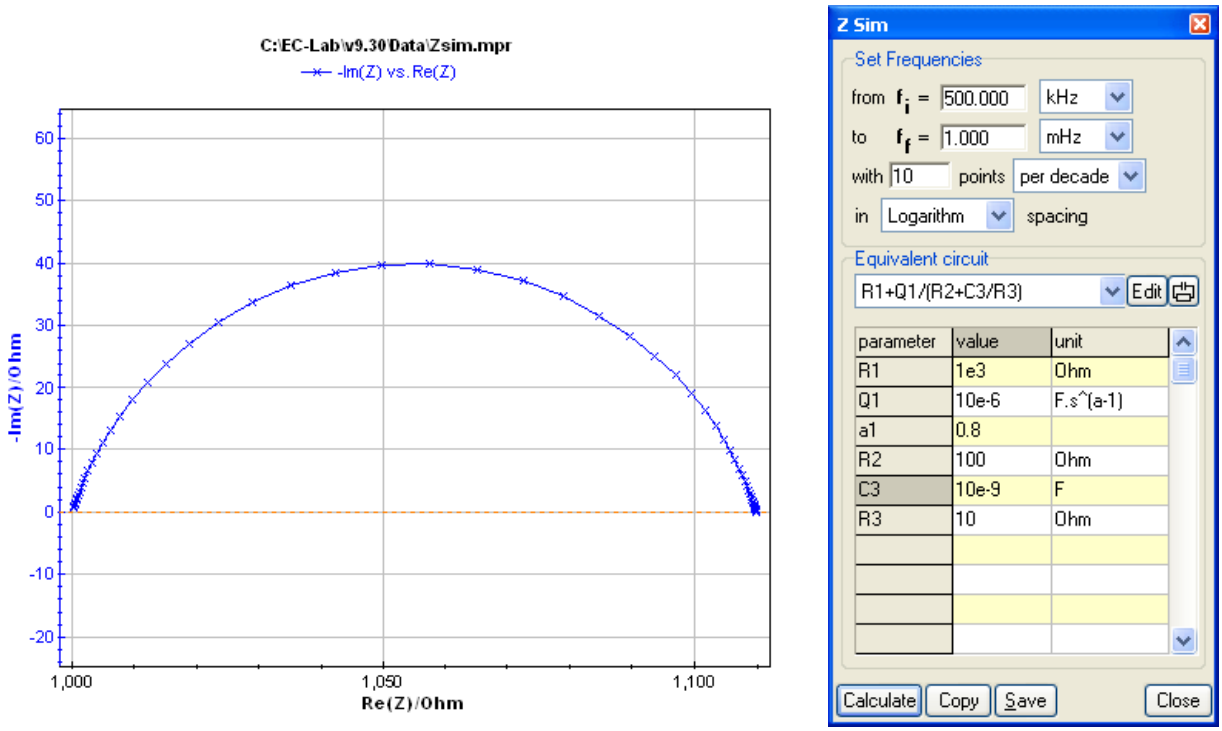


Fig. 146: ZSim menu and the graph corresponding to the selected circuit.

Note: the default opened simulation circuit is the last one used in the previous simulation.

2nd step:

In the frequency frame, set the frequency range (between 500 kHz and 10 µHz) with the number of points per decade and the spacing (logarithmic or linear).

Select an equivalent circuit in the list. If the required circuit is not in the list, then the user can create his circuit in the "**Edit**" window. Click on "**Edit**" to display this window.

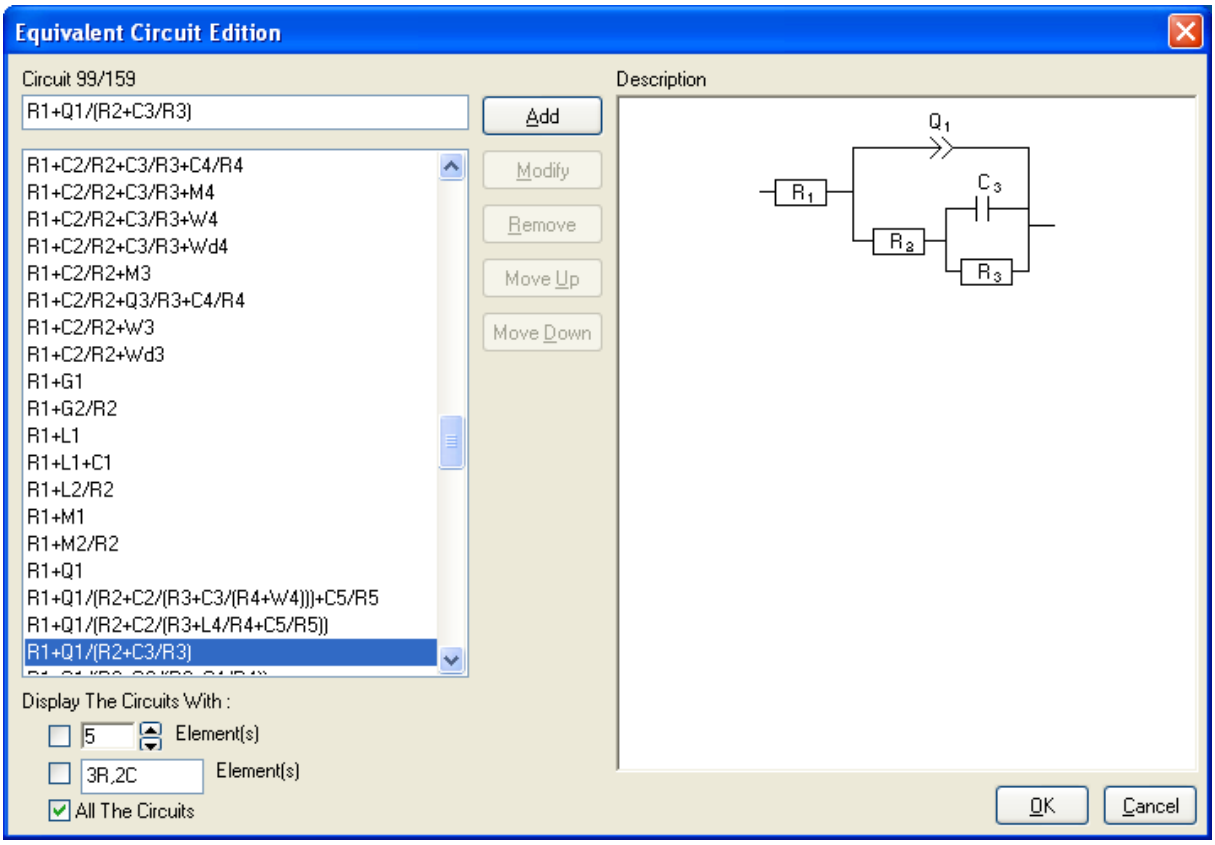


Fig. 147: ZSim/ZFit Circuit Edition window.

The circuit base contains more than 130 circuits. The user can create his circuits to be added (in blue) to the list. The main circuits have been described on the right side of the window (circuit scheme, faradic impedance equation and impedance Nyquist diagram).

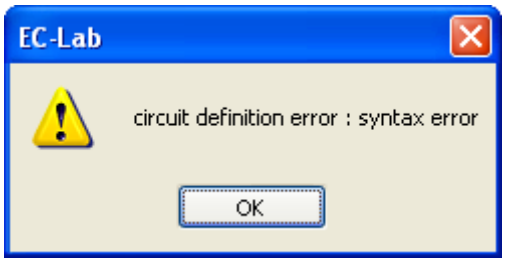
3.4.3.2.2 Circuit selection

To select a circuit in the list the user can select the displayed circuits according to the number of elements or the specific elements in the circuit (number of resistances, number of capacitors, …).

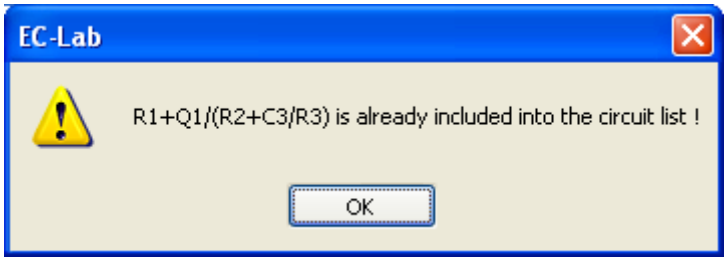
3.4.3.2.3 Description code

If the required circuit doesn't appear in the list, the user can create it. He must write it in the first frame (top) with several rules.

1- For elements in series the used sign is "**+**". For example for R in series with C the equivalent circuit will be "**R1+C1**".
2- For elements in parallel the sign is "**/**". For example for R in parallel with C the equivalent circuit will be "**R1/C1**".
3- If several elements are in series or parallel with each other, then the considered elements must be set between brackets. For example for R2 and C2 in series together and in parallel with R1, the equivalent circuit will be "**R1/(R2+C2)**".
4- To write circuits, it is necessary to give a number for each element to separate the different elements. If the syntax is not correct, an error message will be displayed:



5- If the new circuit is already in the list, this message will appear:



6- Circuits created by the customer will be stored in the list in blue. They can be modified, removed from the list or moved in the list.

7- For the selected file (ZPOT_Fe_basique.mpr), find the correct circuit (Randles Circuit):

R1+Q2/(R2+W2)

8- Click on “Calculate” to show the corresponding curve on the graphic window.

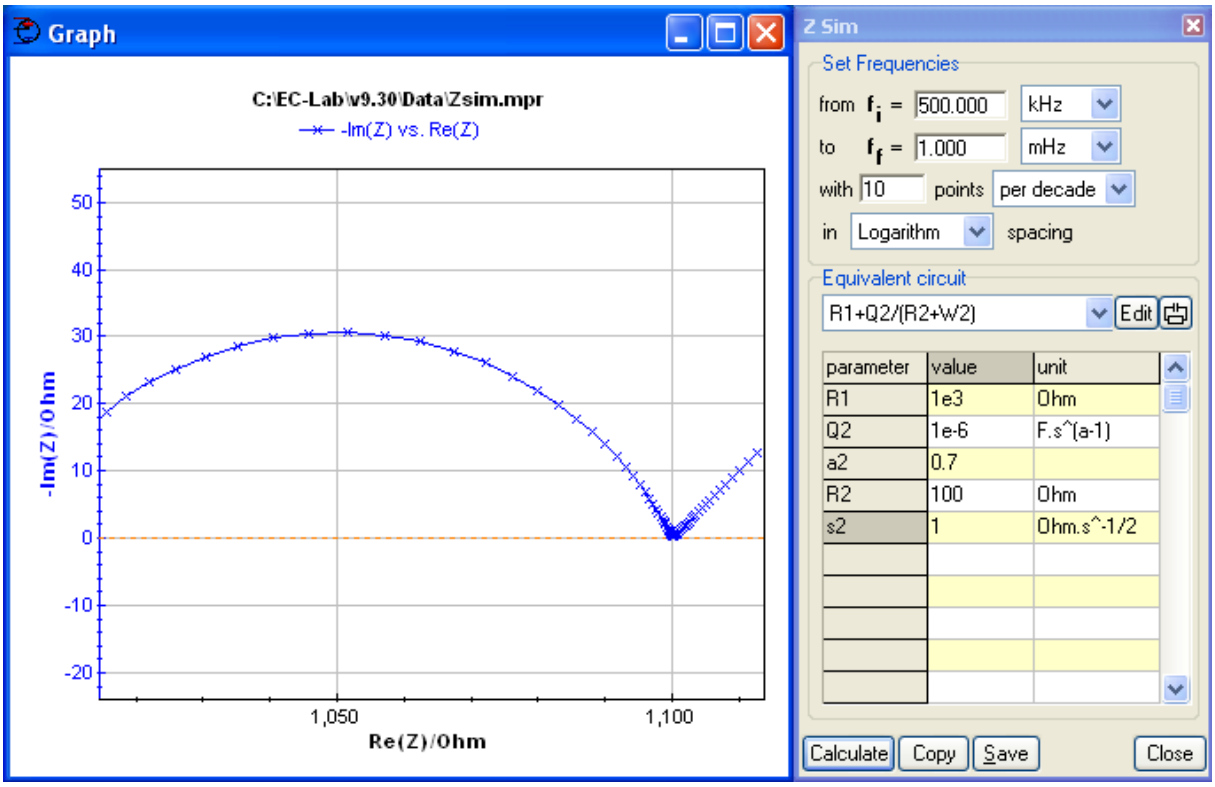


Fig. 148: ZSim Circuit Edition window.

9- To adjust this curve to the experimental one, the user must adjust values for each parameter as described in the window below and click on “**Calculate**”.

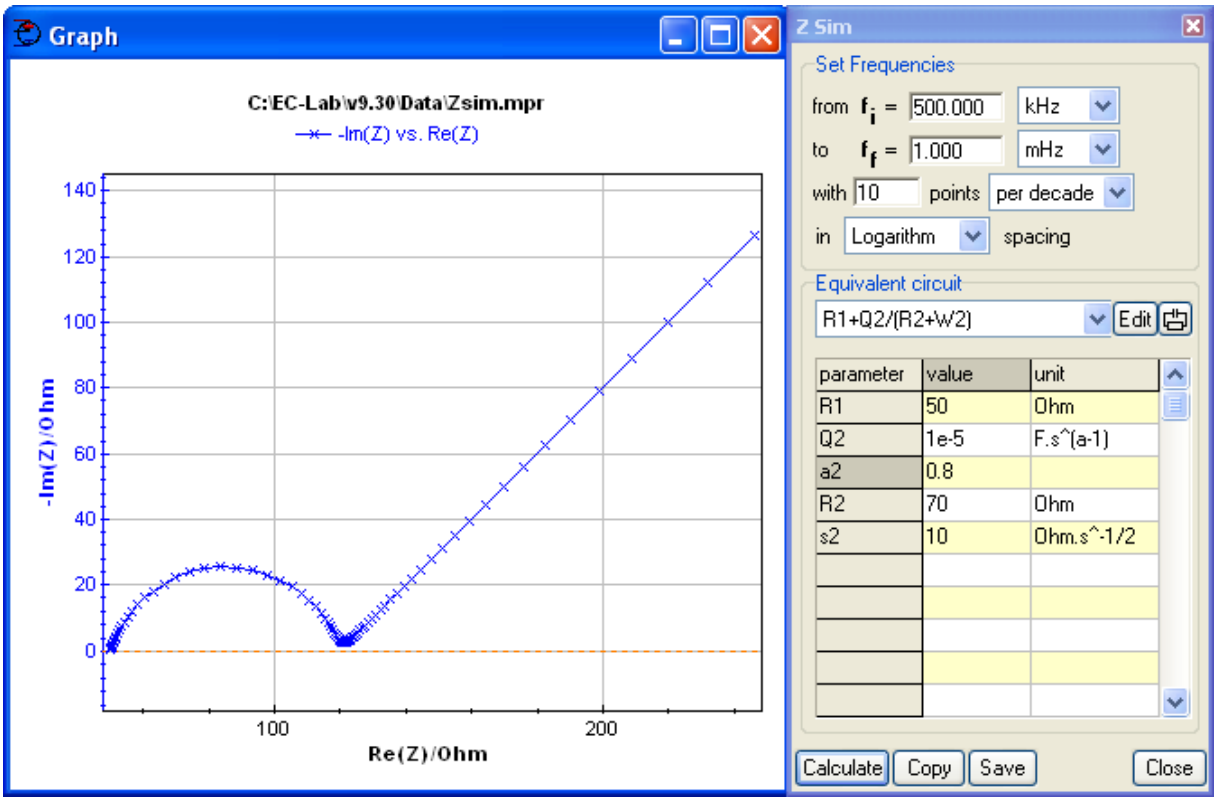


Fig. 149: ZSim Circuit Edition window with adjusted parameters.

The results can be copied to the clipboard and saved in a “Zsim.mpr” file. The user can modify parameters as much as he wants in the table. The new parameters will be implemented when clicking on “Calculate”. To store this simulation the user will have to give another name to the data file because a simulation is always created in the Zsim.mpr file.

3.4.3.3 Fitting: ZFit

When the correct equivalent circuit is defined with ZSim, the user can set it in the ZFit window to identify parameters of the elements with the experimental data points.

3.4.3.3.1 Zfit selection window

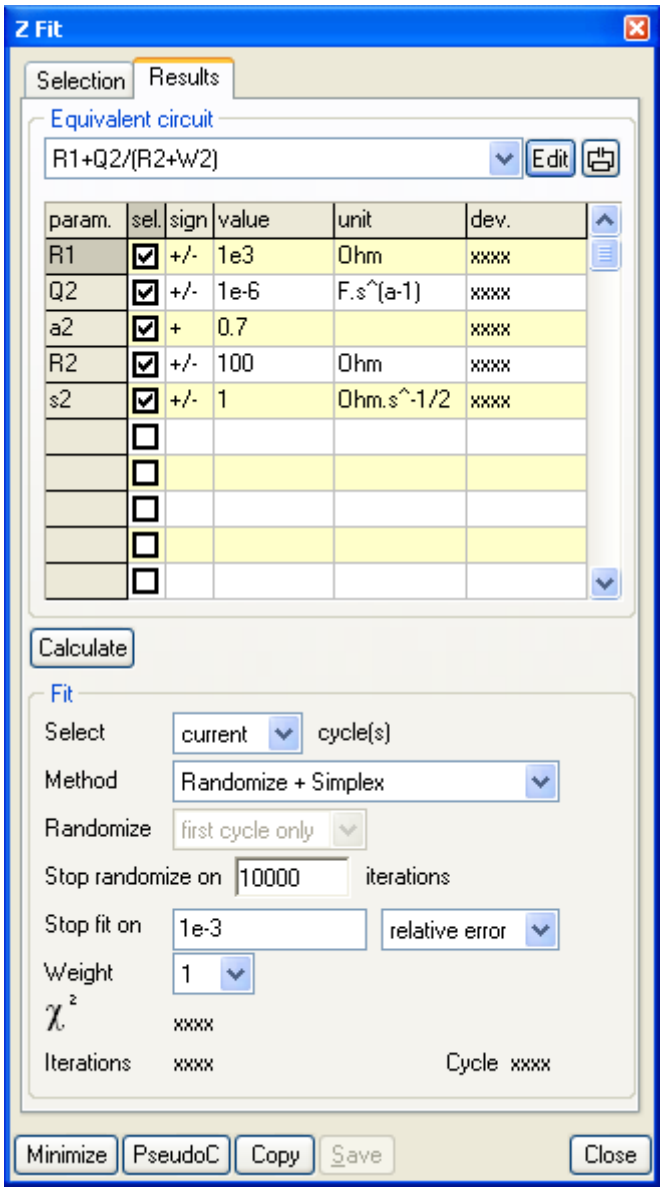


Fig. 150: ZFit Circuit selection window.

As for the Zsim selection window, the Zfit selection window enables the user to edit and create a circuit. For more details about the circuit editing window please refer to the previous section. In the equivalent circuit frame, the table presents each parameter in raw and for each of them, offers the ability to select it in order to be adjusted during the fitting, the ability to define the sign of the value (between +, -, +/-) by double clicking in the box, the unit and the standard deviation calculated when the Levenberg-Marquardt algorithm is used. When the selection box is not ticked the parameter value set in the cell will be considered as the correct value. It will not be modified during the minimization. The **Calculate** button will calculate and plot the data points for the parameter values set in the table without to randomizing or fitting.

3.4.3.3.2 Fitting methods

The Zfit tool can perform successive fits with the same model on successive curves in the same data file. The first thing to be defined by the user is the cycle to do the minimisation (either one fit made on the **current** cycle displayed on the graph or the successive fits made

on **ALL** cycles of the experiment). Default values are set for every parameter, but they never fit properly with the real experimental values. Before to do the fit and in order to help the algorithm to find the best values it is necessary find a couple of values, as close as possible to the real one. Default values too far off will result in a divergence of the algorithm. A randomization has been added before the fitting to select the most suitable couple of parameter values (with the lower χ^2 value). The χ^2 equation used in this method is defined as follows:

$$\chi^2 = \sum_{i=1}^{n} \frac{\left|Z_{meas}(i) - Z_{\text{model}}(f_i, param)\right|^2}{\sigma_i^2}$$

with $Z_{meas}(i)$ is the measured impedance at the f_i frequency,

$Z_{\text{model}}(f_i, param)$ is function of the chosen model,

f_i is the frequency I,

param is the model parameters (ex: R1, R2, C1, Q1, …),

σ_i is the standard deviation. It can be assimilated to the weight of the impedance data points. It can be selected by the user to be 1 or |*Z*|.

Moreover, two fitting algorithms are available and the user can select between the Downhill simplex algorithm and the Levenberg-Marquardt algorithm. Both of them can be tried successively to choose the best results.

In the fitting method the user can select between different combinations:

- only Randomize,
- only Simplex fitting,
- only Levenberg-Marquardt fitting,
- combination of randomize followed by Simplex fitting,
- combination of randomize followed by Levenberg-Marquardt fitting.

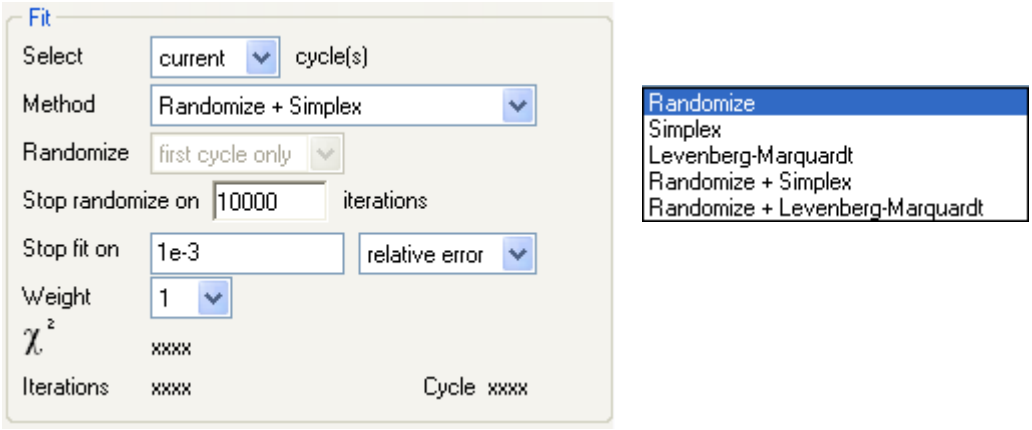


Fig. 151: Fitting method selection.

If **ALL** cycles are selected for the fit, the user will have the possibility of selecting the randomization on the first cycle only or on every cycle.

For both randomisation and fitting, the user can define the **number of iterations** and for the fit he can also select a **relative error**.

Another option, "**Weight**", is available with two choices: either **1** or **|Z|** resulting in a different weight of data points at high and low frequencies. During the fitting process, the iteration number is displayed at the bottom of the window.

To start the operation, click on "**Minimize**".

3.4.3.3.3 Application

Considering the previous example (ZPOT_Fe_basique.mpr), the following result may be obtained using the "**Randomize+Simplex**" option with the default parameter values:

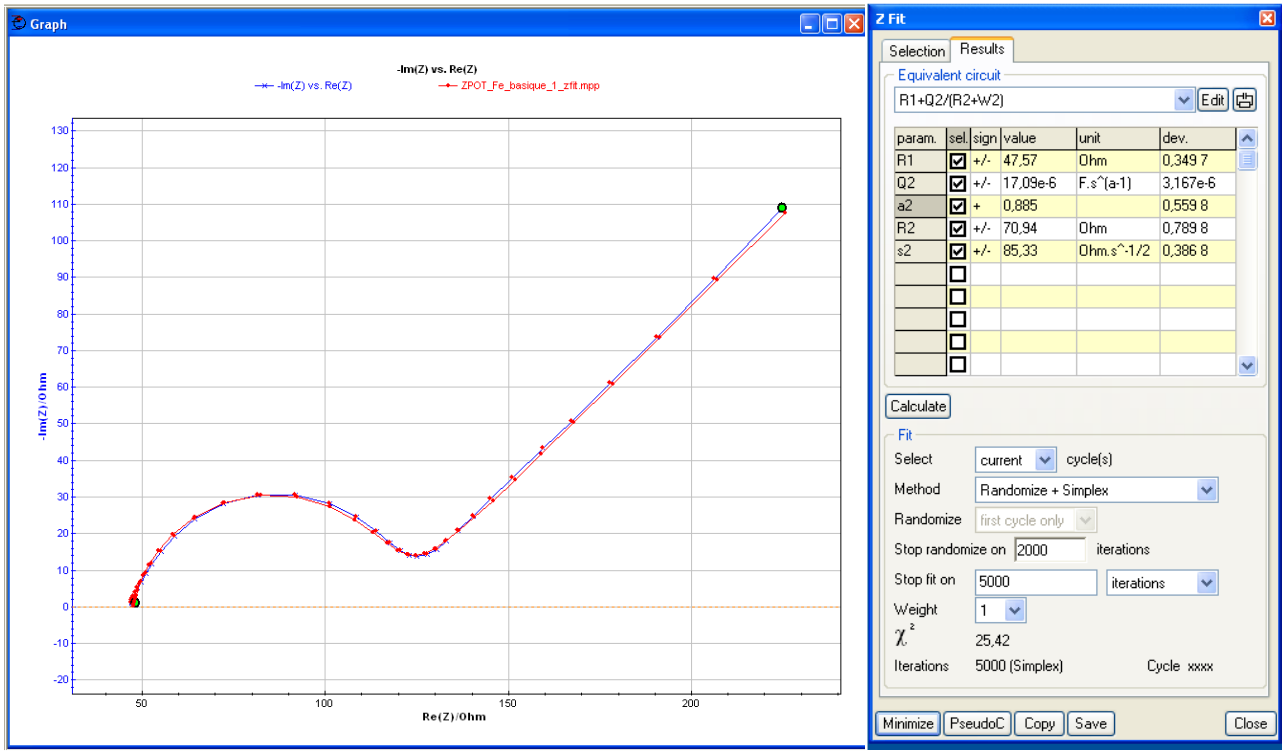


Fig. 152: Fit results with a combination Randomize+Simplex.

The randomization was stopped after 2000 iterations and the fit after 5000 iterations. In that case the χ^2 value is related to a weight 1 for each point. The more the number of points selected for the fit, the higher the χ^2 value will be. In case of a weight |*Z*|, the results are as follows:

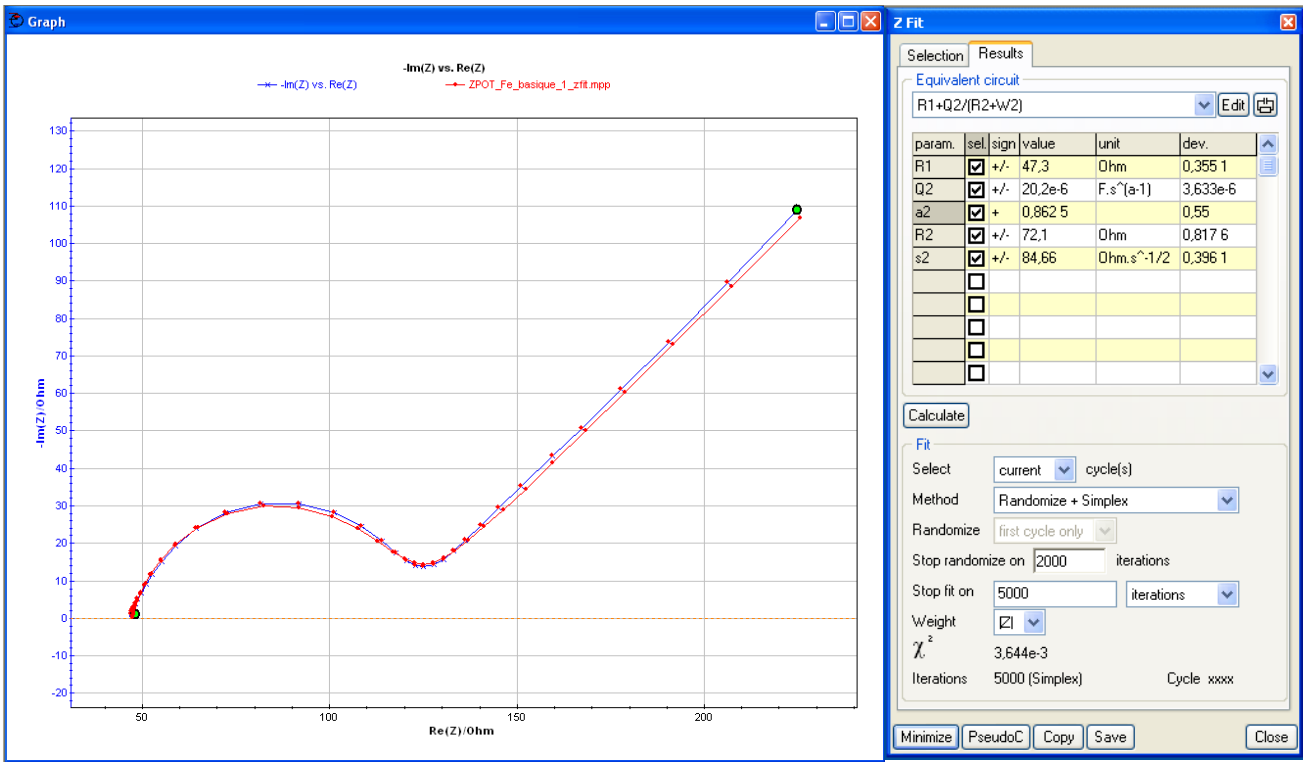


Fig. 153: Fit results with a combination Randomize+Simplex and |*Z*| as weight.

In the case of a weight |*Z*| considered, the χ^2 value tends toward zero. In any case the value must be the smallest possible. The results can be copied to the clipboard or saved in a fit file (filename.fit). When the mpr file is displayed, the fit results can be reloaded with the “Show analysis results” button.
Note that ZFit can be used with data represented with the Bode plot or the Nyquist plot.

3.4.3.3.4 Fit on successive cycles

ZFit tool includes an option to fit successive impedance cycles. For example, in the case of potential steps with EIS measurements on each step we can make an automatic data fitting on each cycle successively without any action by the user. The EIS spectra obtained on each step can be seen on the graph at left hand corner on the figure below. The potential was scanned from 0 to 1 V with 20 steps of 50 mV. We can see the 21 EIS spectra that can be fit one by one at the user’s convenience. Selecting all cycles for the fit and randomisation on only the first cycle will lead to an automatic fit.
When the Minimization is launched a new graph is added at the bottom right hand corner. This graph will display the equivalent circuit parameters obtained by the fit (in this case R1, R2, R3, C2, C3) versus potential or time. The user can have a time evolution or a potential evolution of the desired parameter.

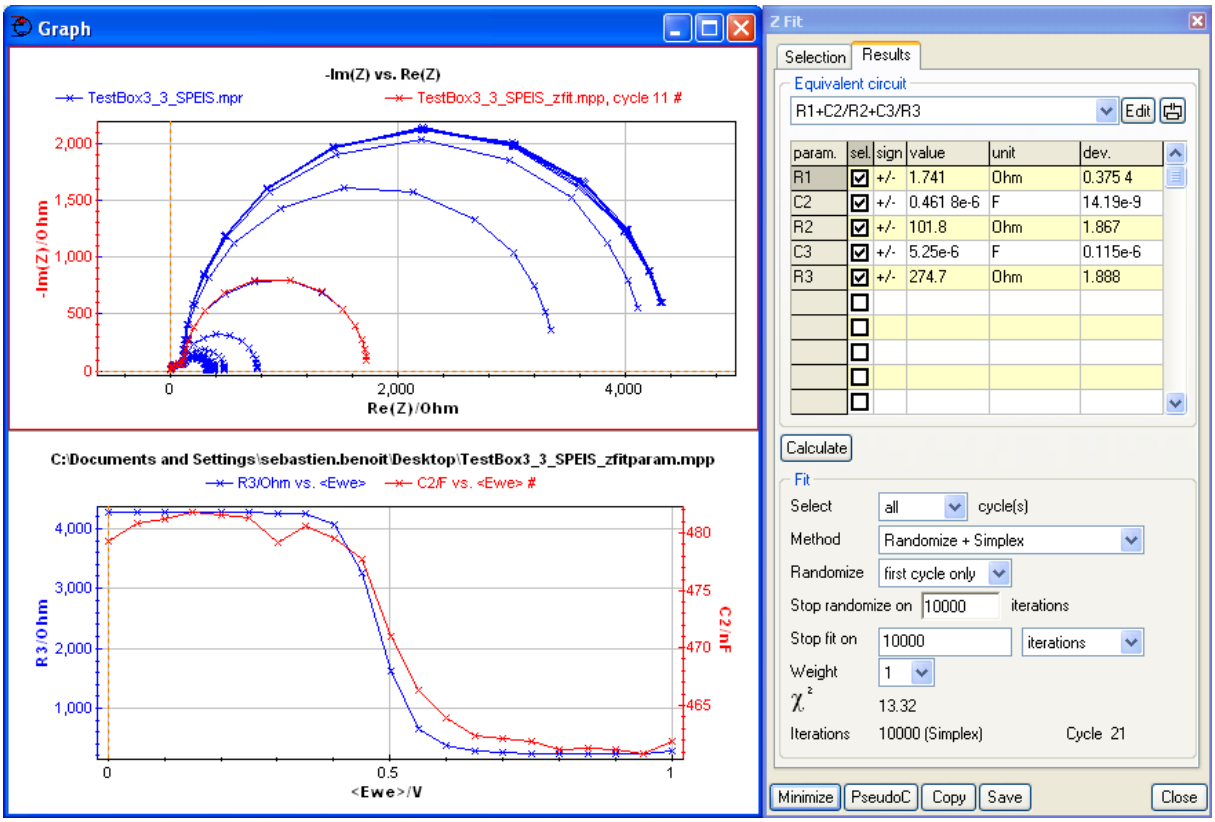


Fig. 154: Successive fits on cycles with randomization on the first cycle.

We can see the potential evolution of the resistance R3 and the capacitance C2. The parameters of the equivalent circuit components are stored for each cycle in the **Filename_Zfitparam.mpp** file.

Note that the fit results are automatically saved in case of multi cycles treatment.

References:

- W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical Recipes in C. The Art of the Scientific Computing, Cambridge University Press, Cambridge (UK), 2nd Edition, 1992.

- E. Walter and L. Pronzato, Identification of Parametric Models: from experimental data, Springer, 2006.

- J.-P. Diard, B. Le Gorrec, C. Montella, Cinétique électrochimique, Hermann, 1996.

- E. Barsoukov and J. Ross Macdonald, Impedance Spectroscopy: Theory, Experiment and applications, Wiley interscience, 2nd Edition, 2005.

3.4.3.3.5 Pseudo-capacitance

ZFit calculates the pseudo-capacitance associated with a CPE. This value can be calculated only for an equivalent circuit R1+(R/Q). This calculation corresponds to the determination of a capacitance value C at a frequency f_0 corresponding to the maximum imaginary part on the Nyquist circle obtained by fitting with the equivalent circuit R1+(R/Q). This value is the solution of the following equation

$$\frac{1}{2\pi(RQ)^{1/\alpha}} = \frac{1}{2\pi RC}$$

with α and Q the CPE parameters. :
Considering the previous example from the first frequency down to 20 Hz, the equivalent circuit could be R1+(R2/Q2)

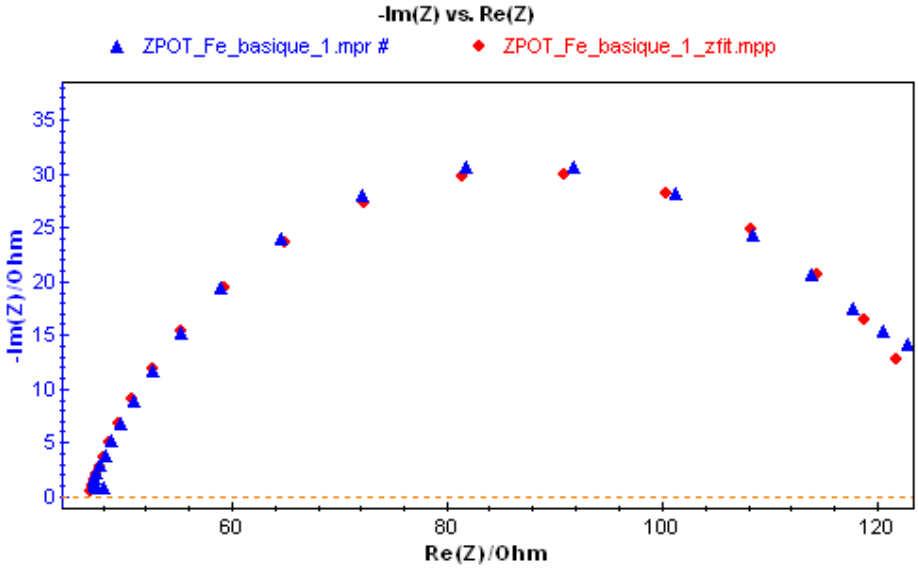


Fig. 155: Fit results with an R1+(R2/Q2) circuit.

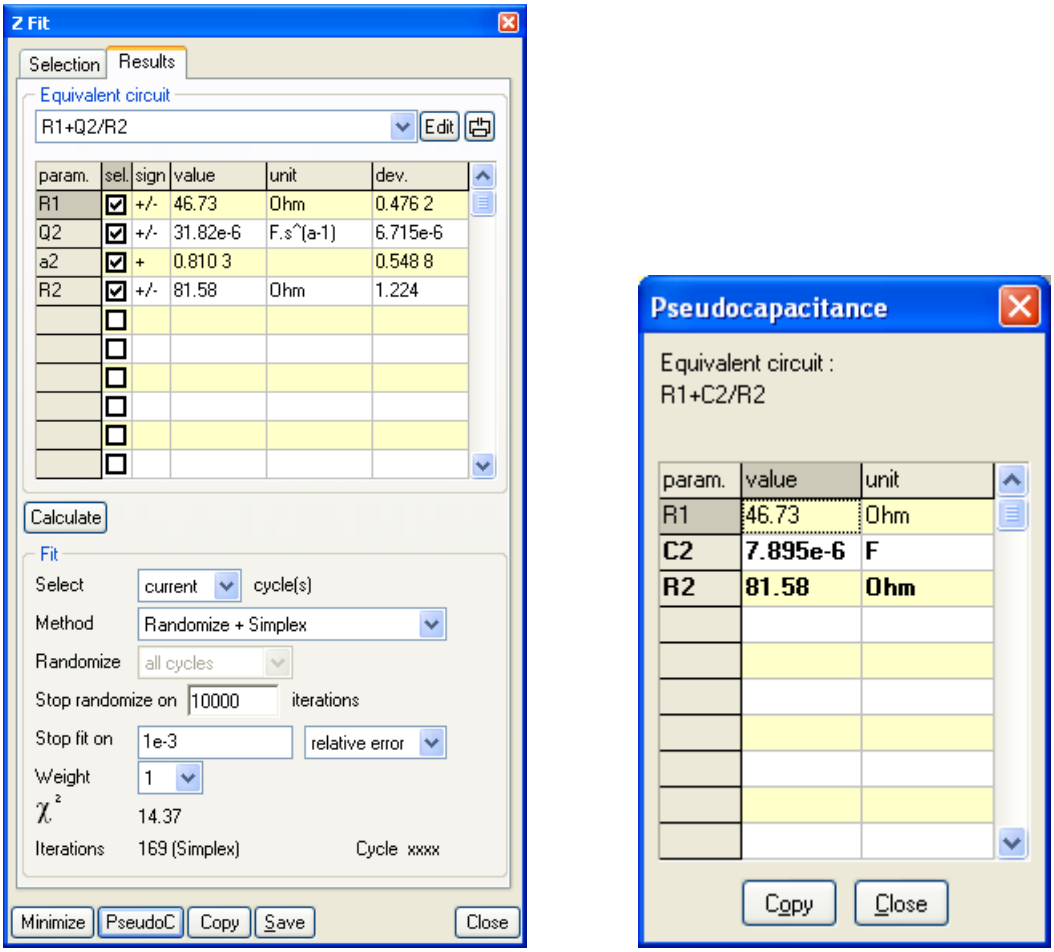


Fig. 156: Fit results and pseudo-capacitance calculation.

The results can be copied and pasted in another document.

3.4.3.3.6 Additional plots

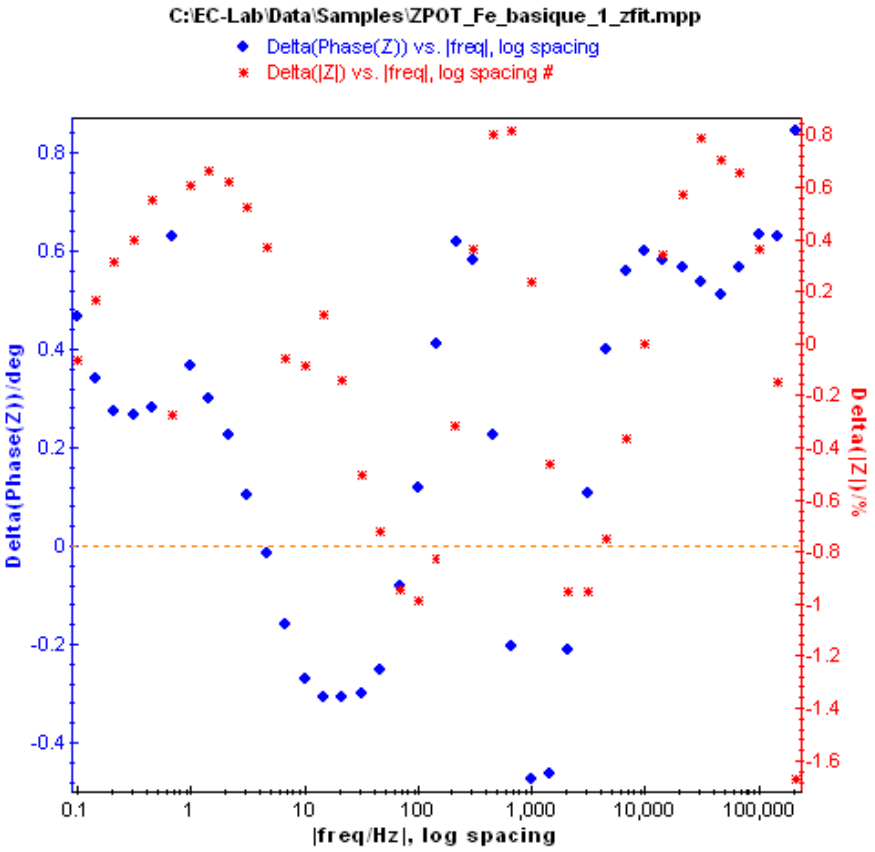


Fig. 157: Plot of the relative error on |Z| and phase vs. frequency (log spacing).

The equations used for this calculation are described below. The same error plot exists for the real part and the imaginary part of the impedance. The error is calculated for each frequency:

$$\Delta|Z|_{\%} = \frac{|Z|_{meas} - |Z|_{calc}}{|Z|_{meas}} \times 100 \; ; \qquad \Delta|\varphi|_{\%} = |\varphi|_{meas} - |\varphi|_{calc} \; ;$$

$$\Delta|\mathrm{Re}(Z)|_{\%} = \frac{|\mathrm{Re}(Z)|_{meas} - |\mathrm{Re}(Z)|_{calc}}{|\mathrm{Re}(Z)|_{meas}} \times 100 \; ; \qquad \Delta|\mathrm{Im}(Z)|_{\%} = \frac{|\mathrm{Im}(Z)|_{meas} - |\mathrm{Im}(Z)|_{calc}}{|\mathrm{Im}(Z)|_{meas}} \times 100$$

Right click on the graph to see the menu and select "**Selector**" to display the following window offering the possibility to display the relative errors. The same window can be accessed from the rapid graphic selection bar (select "**Custom**").

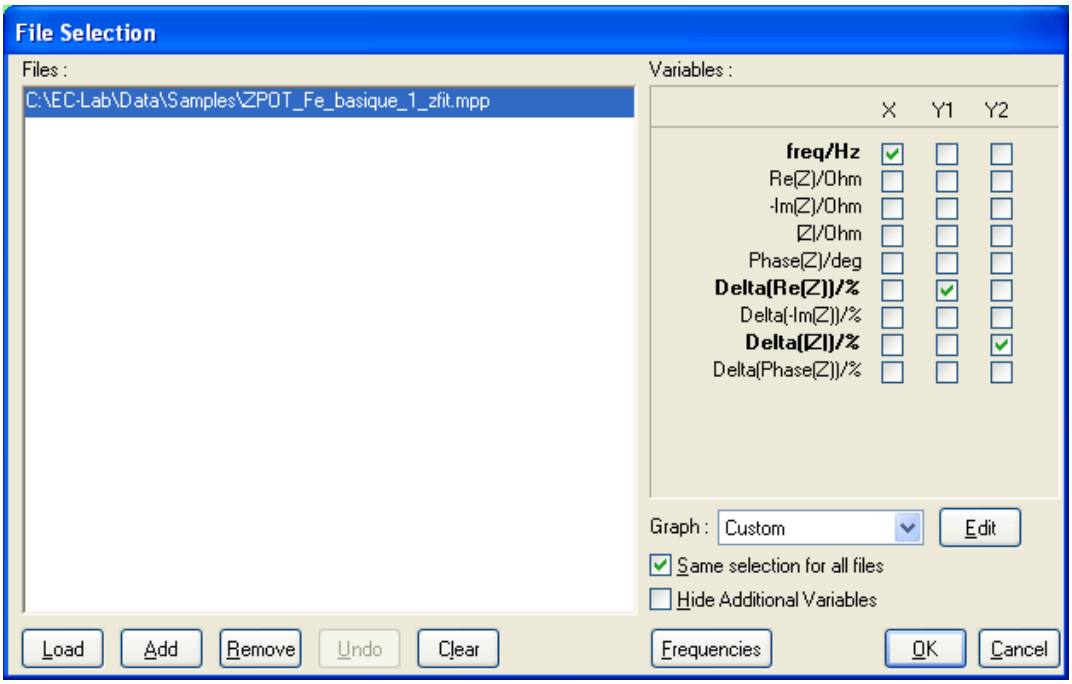


Fig. 158: Selector for the Zfit.mpp file offering the possibility to display the relative errors.

These additional plots may be very useful in evaluating the acceptability of the equivalent circuit selected and the relevance of the measured data points.

3.4.3.4 Mott-Schottky fit

Only the instruments equipped with the EIS measurement option have the capability of Mott-Schottky fitting.

3.4.3.4.1 Mott-Schottky relationship and properties of semi-conductors

The Mott-Schottky relationship involves the apparent capacitance measurement as a function of potential under depletion condition:

$$\frac{1}{C_{SC}^2} = \frac{2}{e\varepsilon\varepsilon_0 N}(E - E_{FB} - \frac{kT}{e})$$

where

C_{sc} is the capacitance of the space charge region,
ε is the dielectric constant of the semiconductor,
ε_0 is the permittivity of free space,
N is the donor density (electron donor concentration for an n-type semi-conductor or hole acceptor concentration for a p-type semi-conductor),
E is the applied potential,
E_{FB} is the flatband potential.

The donor density can be calculated from the slope of the $1/C^2$ vs. E_{we} curve and the flatband potential can be determined by extrapolation to C = 0. The model required for the calculation is based on two assumptions:

a) Two capacitances have to be considered: the one of the space charge region and the one of the double layer. Since capacitances are in series, the total capacitance is the sum of their reciprocals. As the space charge capacitance is much smaller than the

double layer capacitance, the double layer capacitance contribution to the total capacitance is negligible. Therefore, the capacitance value calculated from this model is assumed to be the value of the space charge capacitance.

b) The equivalent circuit used in this model is a series combination of a resistor and a capacitance (the space charge capacitance). The capacitance is calculated from the imaginary component of the impedance (Im(*Z*)) using the relationship:

$$\mathrm{Im}(Z) = -\frac{1}{2.\pi.f.C}$$

This model is adequate if the frequency is high enough (on the order of kHz).

3.4.3.4.2 The Mott-Schottky plot

The Mott-Schottky plot presents $1/C^2$ versus E_{we} or $1/C$ versus E_{we} for each frequency with C calculated from the previous relationship: $\mathrm{Im}(Z) = -\frac{1}{2.\pi.f.C}$.

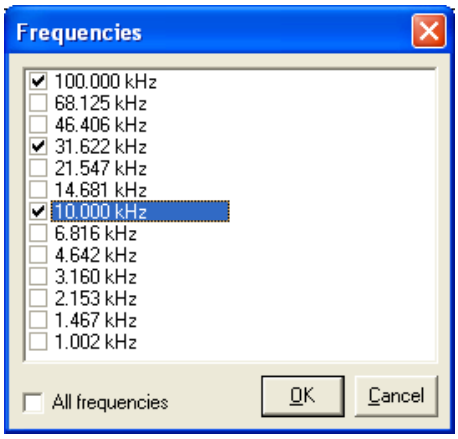


Fig. 159: Mott-Schottky frequency selection window.

When this plot is selected, the window on the left is displayed to select the frequencies. The user can select several or all frequencies. Click on Ok to display the Mott-Schottky curves. The selection is the same for the time evolution of the impedance or of the phase.

Then, the graphic window shows one trace per frequency. Use the shift key to display the frequency.

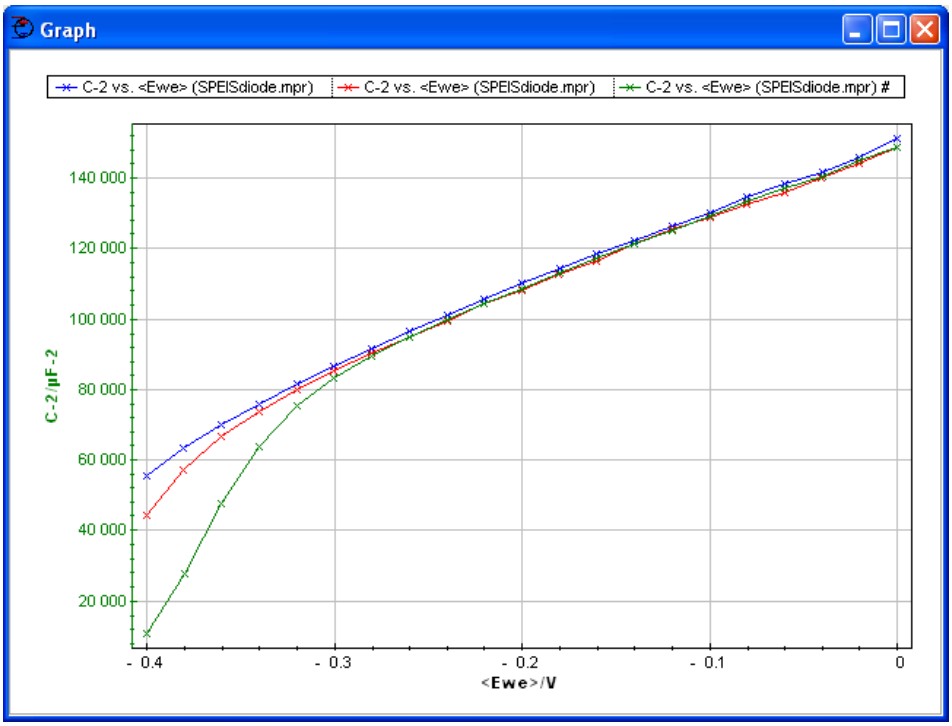


Fig. 160: Mott-Schottky plot.

It is possible to set the surface area and plot a capacitance related to the surface.

3.4.3.4.3 The Mott-Schottky Fit

The Mott-Schottky Fit is a graphic tool introduced with the SPEIS technique to determine semi-conductors parameters (flatband potential and donor density based on the Mott-Schottky relationship) from a Mott-Schottky plot. Before using this fit a Mott-Schottky plot ($1/C^2$ vs. E_{we}) of the experiment must be displayed on the graph. This plot shows one trace for each selected frequency.

The Mott-Schottky Fit corresponds to a linear fit for each trace (one trace for each selected frequency). The same potential range is used for every trace. When a data point zone is selected click on "**Calculate**".

A straight line for each trace is displayed as a result of the linear regression between two green circles with the Least square method fit. Move the circles with the mouse (by holding the mouse left button) to modify the range of data points selected for the fit. The new linear regression is automatically calculated upon moving a circle.

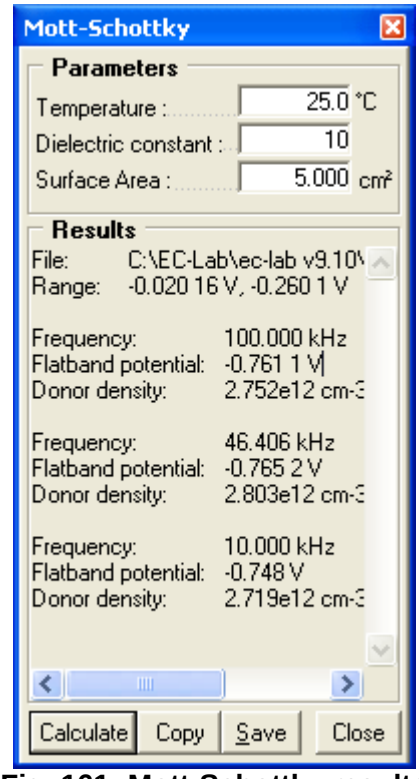


Fig. 161: Mott-Schottky results window.

The potential range used for the analysis is shown in the **Results** frame. For each selected frequency the flat band potential is determined by extrapolation of the linear regression to

C = 0. The donor density is calculated from the slope of the linear regression at 25°C according to the dielectric constant of the material and the surface area of the semi-conductor defined in the **Parameters** frame.

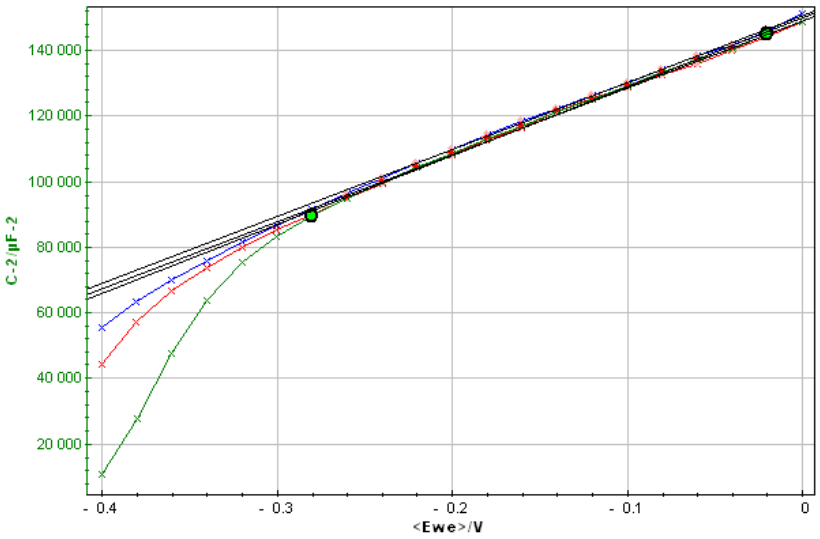


Fig. 162: Mott-Schottky Fit.

The results of the fit (flatband potential, donor density) can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can be saved in a text file.

Other available fit on impedance measurements are developed in the section 3.4.3.1 page 104 of this manual.

3.4.3.4.4 Saving Fit and analysis results

All the fits described above can be saved in a text file. Click on “save” to create a fit file (*.fit) in the same folder as the raw data file. When the data file is displayed a function “**Show Analysis Results …**” is available on the right click menu. Select this function to display the fit results window:

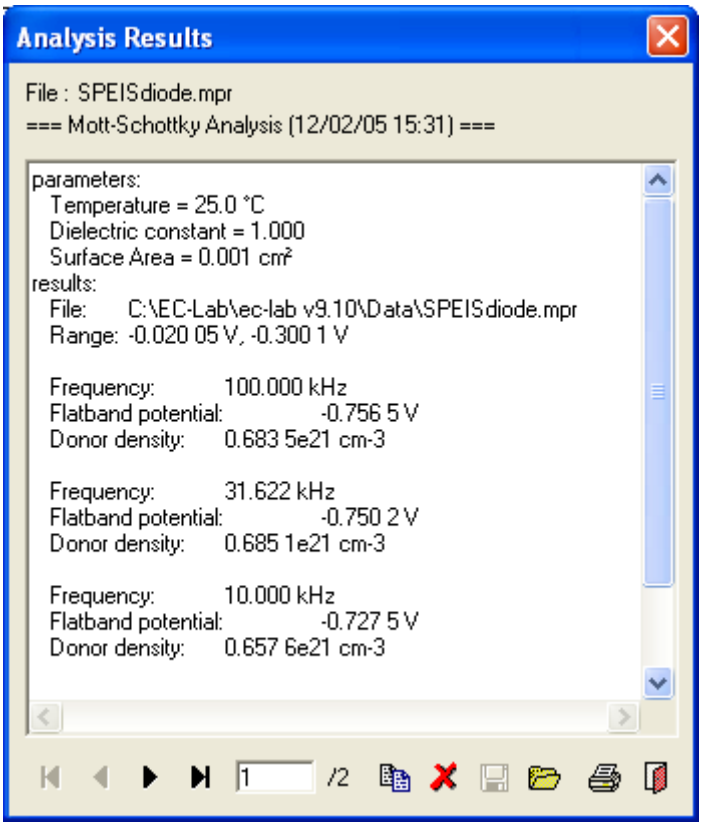


Fig. 163: Analysis Results window.

This text file shows the file name and the analysis performed on the curve with the date and time at the top. If several fits were made successively on the curve, the user can display every analysis one after the other using the "**Next**" button. The results can be printed, edited to be copied, or deleted.

3.4.3.5 Kramers-Kronig transformation

According to several conditions on the studied system, it is possible to determine the imaginary part of the impedance from the real part and vive versa. The system must be causal, stable, linear, and invariant in time and the impedance must be finite when ω→0 or ω→∞. This transformation is sometimes used in electrochemistry for the validation of experimental results. For example the impedance imaginary part can be calculated from the real part (or conversely) with the equation:

$$\mathrm{Im}(Z_{KK}(\omega)) = \frac{2\omega}{\pi}\int_0^{\infty} \frac{\mathrm{Re}(Z(x)) - \mathrm{Re}(Z(\omega))}{x^2 - \omega^2}\,dx$$

The Kramers-Kronig transformation can also be verified in an admittance plot.
If we consider the previous data file (ZPOT_Fe_Basique.mpr), the Kramers-Kronig transformation applied to the whole point series gives the following results:

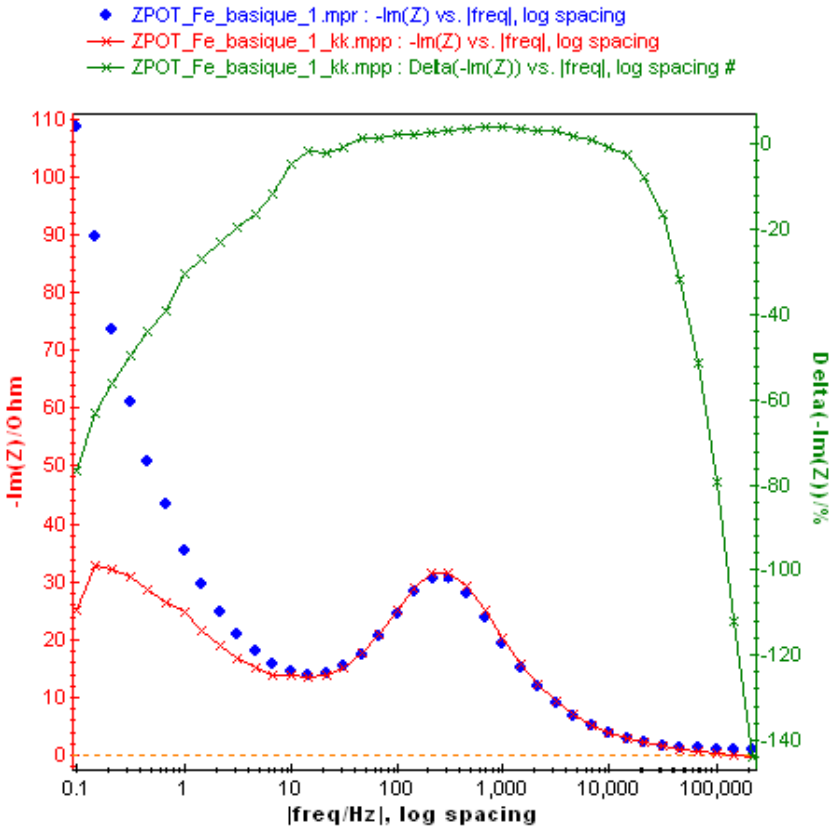
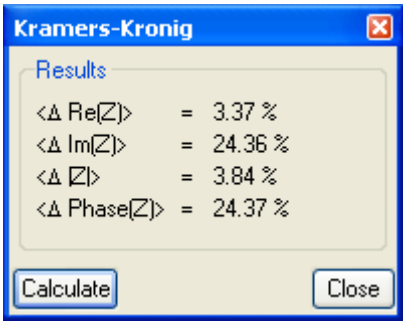


Fig. 164: Result of the Kramers-Kronig criterion applied to the data points with the experimental Im(Z) part, the calculated one and the relative error.

One can see that the Kramers-Kronig criterion is not applicable to this system because in the low frequency range the impedance doesn't tend towards 0. For the high frequency range, the imaginary parts tend to 0. So the precision is not significant.



The results of this test are displayed as an averaged relative error for each parameter (Re, Im, |Z| and phase).

References:

- H.W. Bode, Networks Analysis and feedback Amplifier design, Van Nostrand, New York, 1945.

- R.L. Van Meirhaeghe, E.C. Dutoit, F. Cardon and W.P. Gomes, Electrochim.Acta, 21 (1976), 39.

- D.D. MacDonald, Electrochim. Acta, 35 (1990), 39.

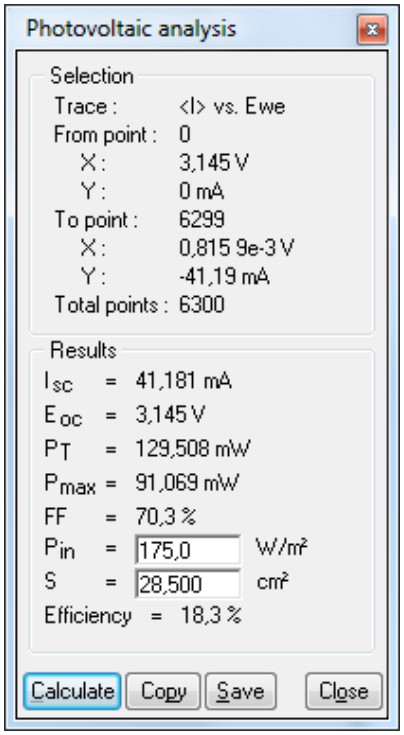
- J.-P. Diard, P.Landaud, J.-M. Le Canut, B. Le Gorrec and C. Montella, Electrochim. Acta, 39 (1994), 2585.

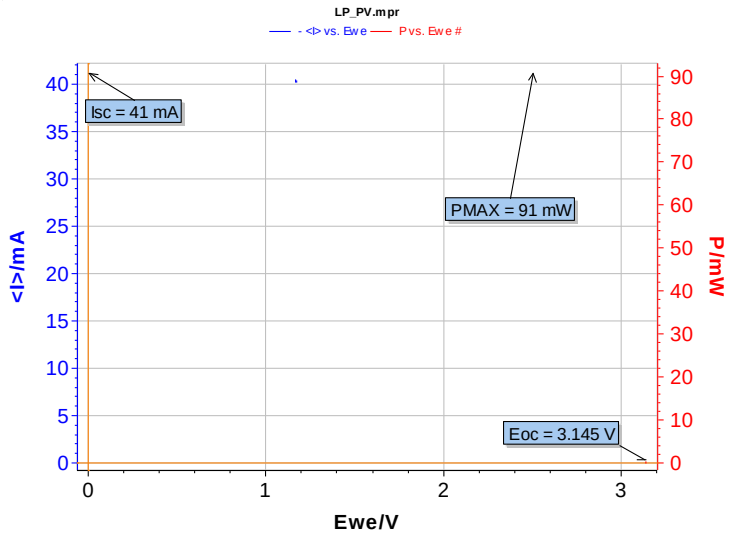
3.4.4 Batteries menu

This menu is only composed of process tools and these processes are described in the paragraph 3.5.

3.4.5 Photovoltaic/fuel cell menu

The photovoltaic analysis provides characteristic values of a solar cell.





The resulting *I-V* characterization shows a typical *I vs. E* and *P vs. E* curves. Several parameters can be drawn from this curve with the “Photovoltaic analysis” tool:

- Short Circuit Current (I_{sc}), which corresponds to the maximum current when E = 0 V, I_{sc} = 41 mA in this example,
- the Open Circuit Voltage (E_{oc}), which is the potential when the current is equal to zero ampere, E_{oc} = 3.145 V,
- the theoretical power (P_T), which is defined by the following relationship $P_T = I_{sc} \times E_{oc}$, P_T = 129 mW,
- the maximum power, P_{MAX} = 91 mW,
- the fill factor (FF), which is the ratio of P_{MAX} and P_T, FF = 70.3%,
- the efficiency can also be calculated. If we assume that the solar power is equal to the means of the surfacic solar power (175 W/m^2), which is 499 mW for our photovoltaic cell surface area (28.5 cm^2). The efficiency of the solar cell is 18%.

3.4.6 Corrosion menu

Several techniques such as Linear Polarization (LP), Constant Amplitude Sinusoidal microPolarization (CASP) and Variable Amplitude Sinusoidal microPolarization (VASP) measurements are used to characterize the corrosion behavior of metallic sample. These measurements yield to determine the characteristic parameters such as:

- the corrosion potential, E_{corr},
- the corrosion current, I_{corr},
- the Tafel constant for the anodic, β_a (metal oxidation) and cathodic β_c (oxidant reduction) reactions and are defined as positive numbers. Tafel constant can be given as b_a and b_c where $b_a = \ln 10/\beta_a$ and $b_c = \ln 10/\beta_c$.

The "Corr Sim" tool allows user to simulate data. All these methods are based on the Stern and Geary model. Stern and Geary (ref. [1]) proposed a model of a corroding system that involves two electrochemical reactions, an oxidation process and a reduction process. This model is based on the Tafel equation that predicts that the logarithm of the current observed in an electrochemical process is directly related to the difference between the applied potential and the open circuit potential.

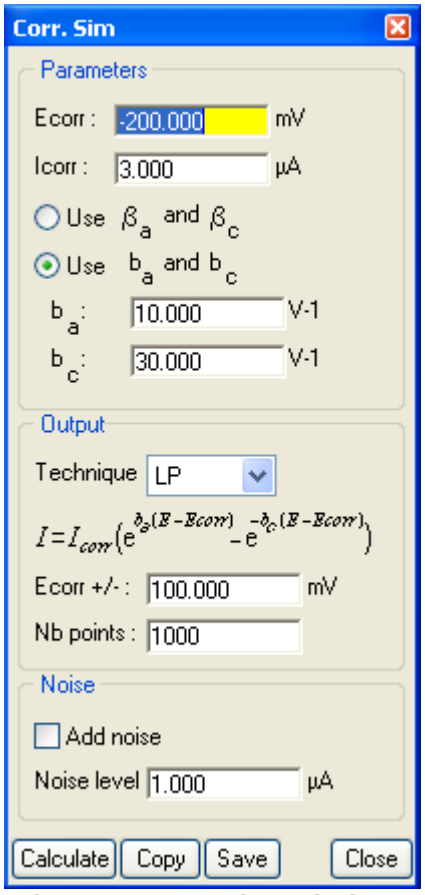


Fig. 165: Corr. Sim. window.

The Stern equation can be expressed as follow:

$$I(E) = I_{corr}\left(10^{\frac{E-E_{corr}}{\beta_a}} - 10^{\frac{E-E_{corr}}{\beta_c}}\right)$$

where I(E) is the total current at a specific applied potential E. E_{corr} is the open circuit potential of the system. β_a and β_c are the Tafel constant for the anodic (oxidation) and cathodic (reduction) reactions and are defined as positive numbers.
I_{corr} is the corrosion current corresponding to the anodic and cathodic current at $E = E_{corr}$. The total current $I(E_{corr})$ resulting into the difference of the anodic and cathodic current being null as expected.

The three proposed methods are presented hereafter. The appropriate method has to be selected in the combo box of the output frame.

Noise in current, in potential or in resistance depending on the technique can be superimposed to the resulting simulated data.

Clicking on the "Calculate" button gives the simulated curve according to the parameters set. The ouptut plot depends on the type of the techniques used. The results can be copied in the clipboard to be pasted in the print window comment zone or in a text file. They can be saved in a text file.

Reference:

[1] Stern M. and Geary A.L., J. Electrochem. Soc., 104, (56), 1957.

3.4.6.1.1 Linear microPolarization (LP)

Among all the techniques offered, the linear micropolarization is the most standard one. Resulting plot is given in I *vs.* E. For this modeling, the range of potential scan around the corrosion potential and the number of points are set.

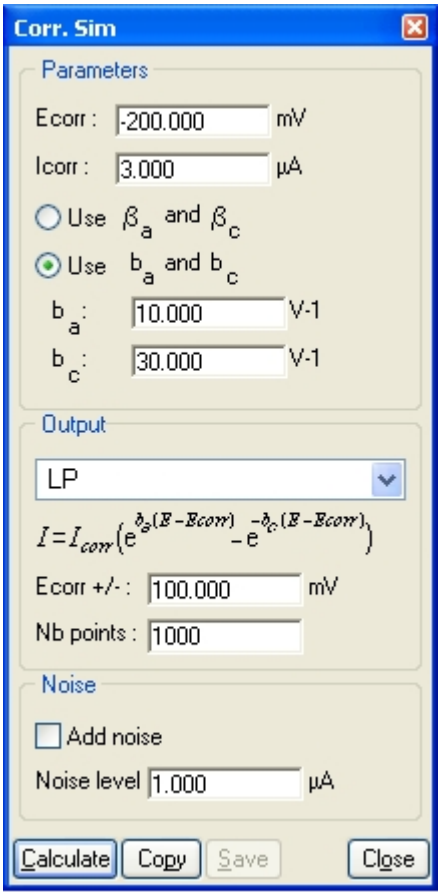


Fig. 166: Corr Sim window for Linear Polarization.

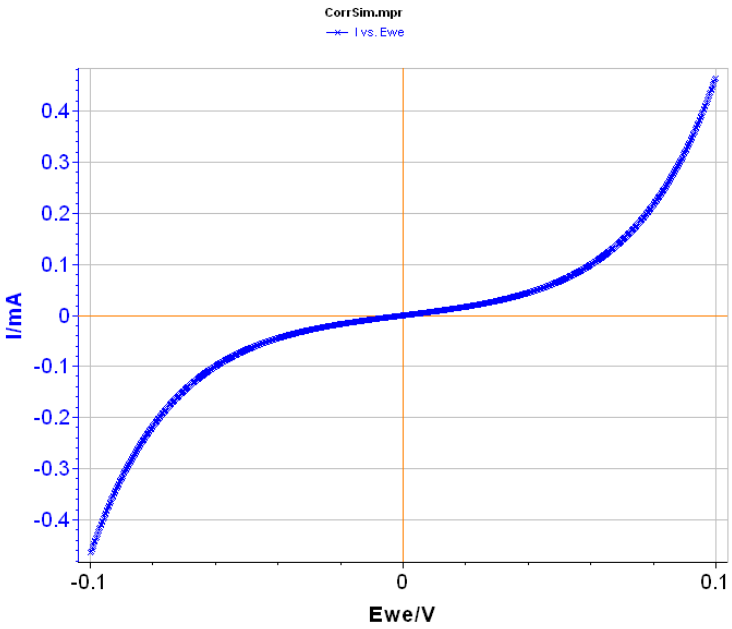


Fig. 167: Output data for Linear Polarization simulation.

3.4.6.1.2 Constant Amplitude Sinusoidal microPolarization (CASP)

In this technique, a small sinusoidal excitation is applied to the system. In order to prevent the polarization of the sample, the intensity of the excitation (V_a) has to be weak, for example few mV. The frequency of the sinus (f_s) is typically in the hertz range. The simulated harmonic plot is given in I vs. Time.

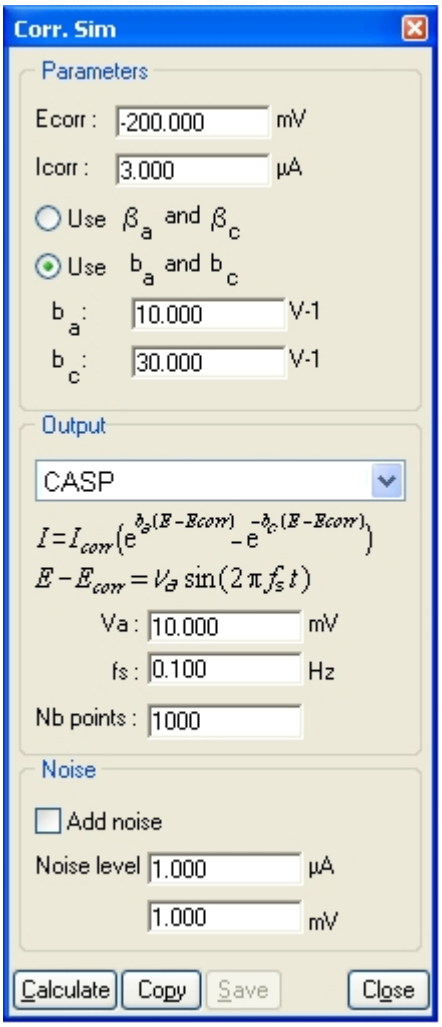


Fig. 168: Corr Sim window for CASP Simulation.

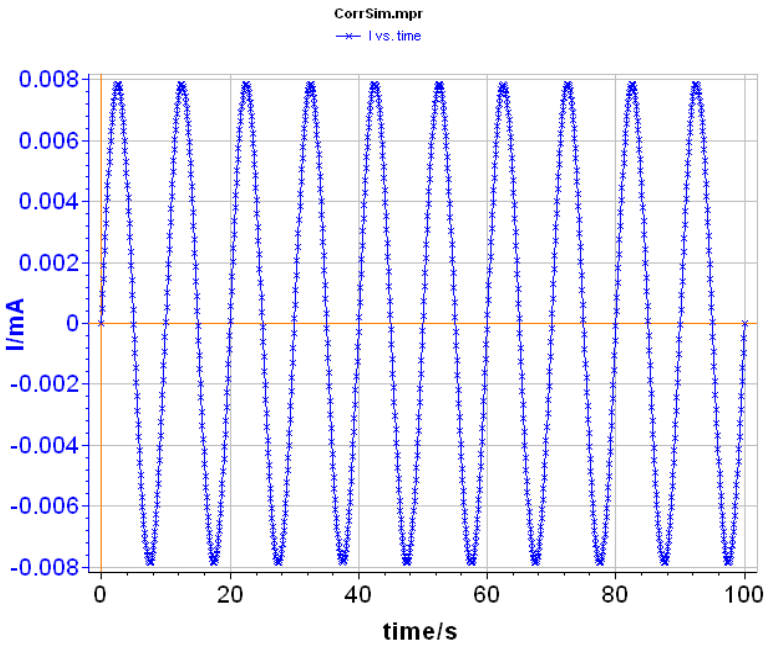


Fig. 169: Output data for CASP simulation.

3.4.6.1.3 Variable Amplitude Sinusoidal microPolarization (VASP)

The R_p determination is done at several sinus amplitude from Va min to Va max. These measurements are typically performed at low frequency. Variable amplitude EIS simulated plot is given in R_p *vs.* sinus amplitude. Regarding the settings, the simulation required the range of frequency and the number of point.

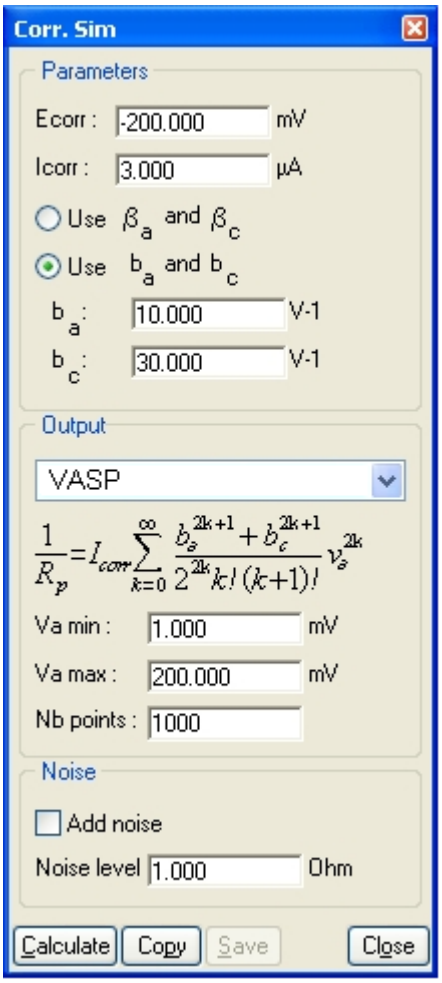


Fig. 170: Corr Sim window for VASP Simulation.

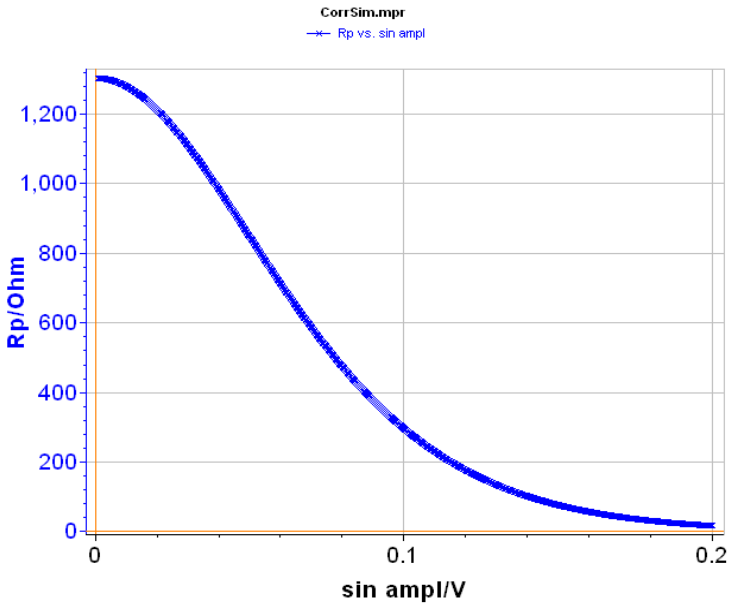


Fig. 171: Output data for VASP simulation.

3.4.6.2 R_p Fit

For E sufficiently close to E_{corr}, it is possible to simplify the Stern and Geary equation, such as

$$I = I_{corr}(E - E_{corr})\frac{\beta_a + \beta_c}{\beta_a \beta_c}\ln 10$$

This equation is commonly presented with E as function of I:

$$E = \frac{I\beta_a\beta_c}{I_{corr}(\beta_a + \beta_c)\ln 10} + E_{corr}$$

When expressed this way it is easy to see that E = E_{corr} for I = 0. The slope of this equation is termed the *polarization resistance* because it has the unit of a resistance and is commonly abbreviated R_p:

$$\text{Polarization resistance} = R_{p,E_{corr}} = \frac{\beta_a\beta_c}{I_{corr}(\beta_a + \beta_c)\ln 10}$$

For the **R_p Fit**, the user has to select the data points and the fit (with the R_p fit button as described before). Then click on "**Calculate**". The software will automatically find a potential value E_1 on the curve for I = 0. Two circle markers are set in a ± 25 mV potential range around E_1. This range and β_a and β_c values used for the fit are defined in the **Parameters** frame.

The **R_p Fit** calculates the polarization resistance (R_p) and the open circuit potential (E_{corr}) by a linear regression around E_1 (± 25 mV) on I vs. E plot. All the data points in the potential range are used for the linear regression.

R_p is given by the inverse of the linear fit slope and E_{corr} by the potential value calculated from the linear equation for I = 0.

The correlation coefficient shows the accuracy of the linear regression.

It is also possible to determine I_{corr} by adjusting the Tafel coefficients β_a and β_c previously determined by the Tafel Fit.

The results can be copied to the clipboard to be pasted in the print window comment zone or in a text file. They can also be saved in a text file.

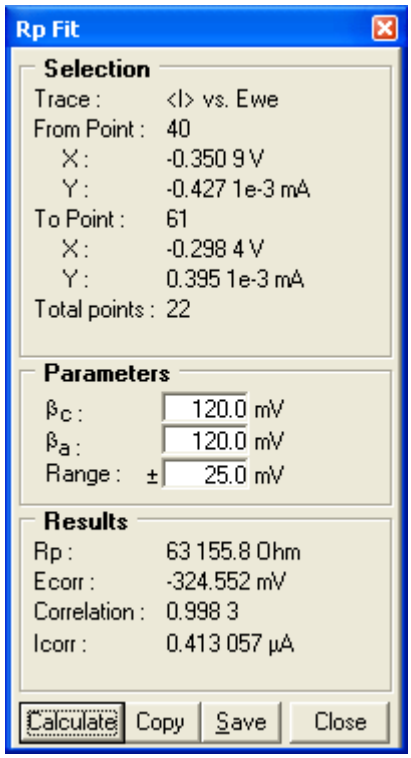


Fig. 172: R_p Fit window.

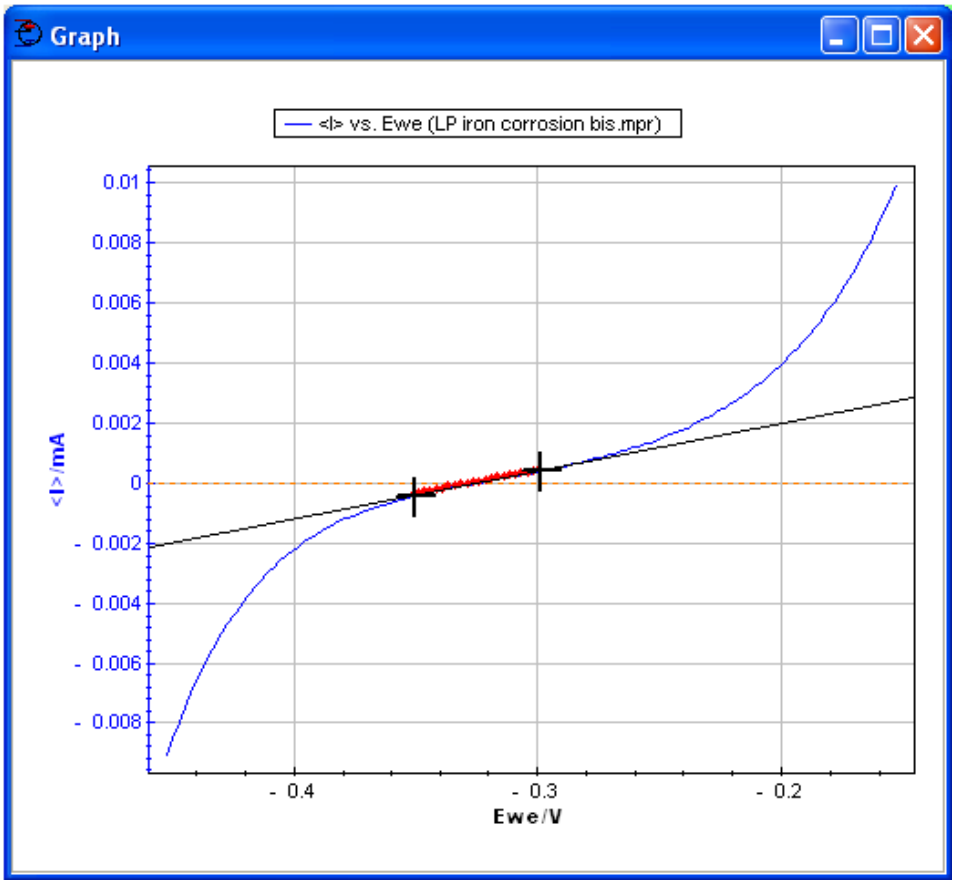


Fig. 173: Linear polarization curve of an iron electrode in H_2SO_4 (0.1 M).

Note: - The user can adjust the R_p Fit. He must grab and move markers. The fit result is automatically updated. It is not necessary to click on “Do fit” again.

- One could use the Linear fit to get the same results, but the R_p fit is more convenient for the R_p calculation.

3.4.6.3 Tafel Fit

The Stern and Geary equation predicts that for $E > E_{corr}$ the anodic reaction predominates and that for $E < E_{corr}$ the cathodic reaction predominates:

$$I \approx I_{corr} 10^{\frac{E-E_{corr}}{\beta_a}}, \qquad \text{for } E > E_{corr}$$

$$I \approx -I_{corr} 10^{\frac{E-E_{corr}}{\beta_c}}, \qquad \text{for } E < E_{corr}$$

So, in a log|I| versus E representation, one should see two linear parts for $E > E_{corr}$ and $E < E_{corr}$:

$$\log|I| \approx \frac{E-E_{corr}}{\beta_a} + \log I_{corr}, \qquad \text{for } E > E_{corr}$$

$$\log|I| \approx \frac{E_{corr}-E}{\beta_c} + \log I_{corr}, \qquad \text{for } E < E_{corr}$$

3.4.6.3.1 Tafel Fit window

The **Tafel Fit** window allows the user to find the anodic and cathodic Tafel coefficients into a log(|I|) versus *E* representation (Tafel Graph).

On a linear polarization trace, select the **Tafel Fit** with the Tafel Fit button or the mouse right click and the data points where the fit will be performed. The Tafel Fit analysis window appears (Fig. 175). The user will receive a warning message to switch to the log(|I|) versus E_{we} graph representation.

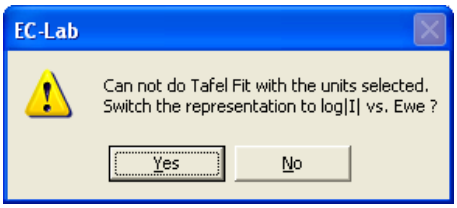


Fig. 174: Tafel Fit warning message to switch the graph representation.

Answer **Yes** to the previous message. The fit can be minimized with a simplex method.

The results can be copied to the clipboard to be pasted in the print window comment zone or a text file. They can also be saved in a text file.

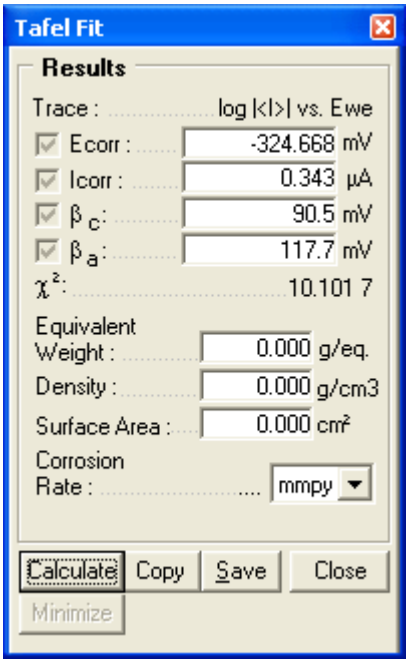


Fig. 175: Tafel Fit window.

Note: - One can manually select the log(|I|) versus E representation. In **graph properties/axis/axis processing**, select “**log |I|**” for Y1.

- The equivalent weight, the density and the surface area used for the corrosion rate calculation can be defined before the beginning of the experiment in the "**Cell characteristics**" window.

The Tafel graph (Fig. 176) is displayed in $\log|I|$ vs. E_{we}. Two linear regressions are automatically made using the least square method. Each linear fit is limited with two circle markers that can be moved.

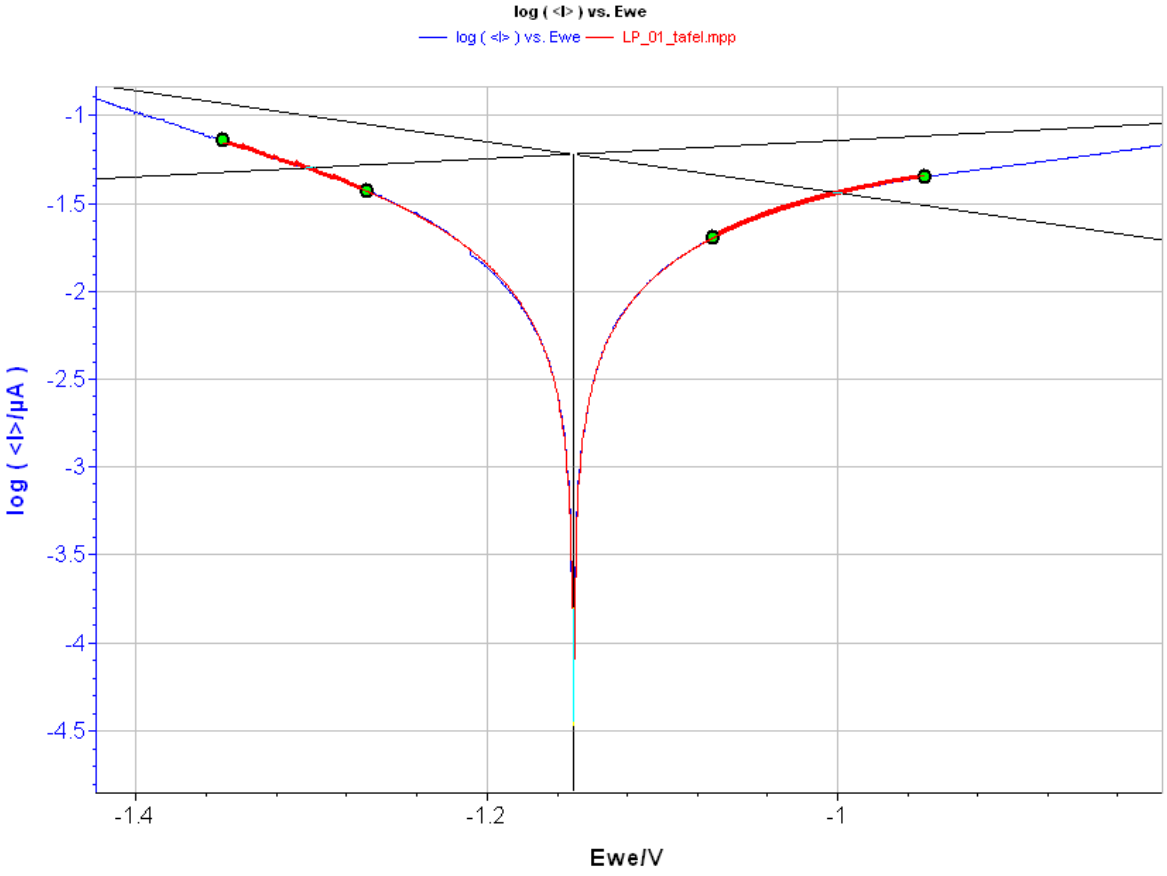


Fig. 176: Tafel graph.

Results of the Tafel Fit are calculated whenever a marker is moved. The default positions of the markers are ± 80 mV and ± 200 mV around $E_{I=0}$. The software deduces the open circuit potential (E_{corr}) to linear regressions intersection, the corrosion current value (I_{corr}) and the Tafel constants (β_a and β_c). The Fit accuracy can be estimated with the χ^2.
The Tafel Fit also works with the plot Ewe vs log|I|

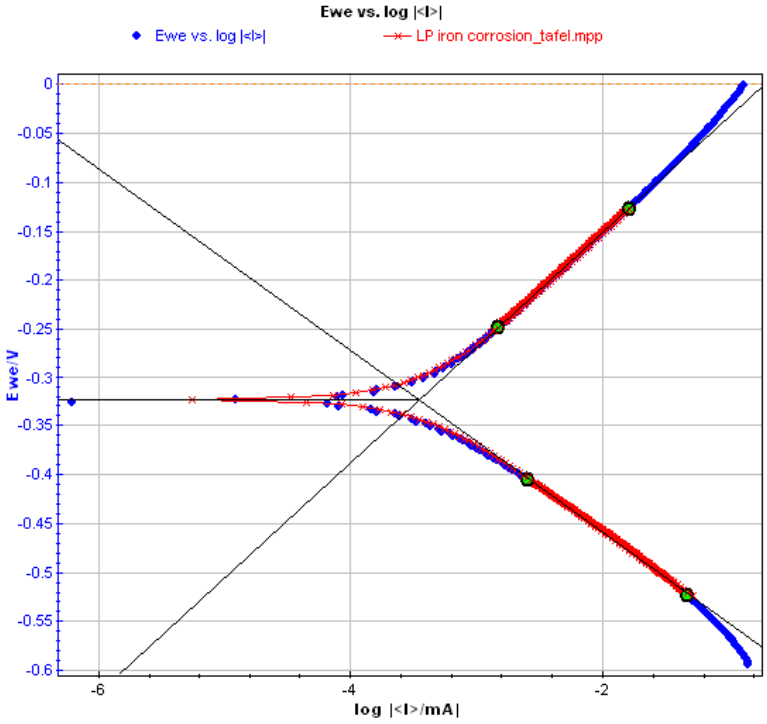


Fig. 177: Tafel Fit on the Ewe vs log|I| graph.

3.4.6.3.2 Corrosion rate

Finally the corrosion rate (CR) is calculated according to the next equation:

$CR = \frac{I_{corr}.K.EW}{d.A}$ in millimeter per year (mmpy) or milliinches per year (mpy)

I_{corr}	corrosion current (in A).
K	constant that defines the units of the corrosion rate.
EW	equivalent weight (in g/equivalent).
d	density (in g/cm^3).
A	sample area (in cm^2).

K	CR units
3272 mm/(A-cm-year)	mm/year (mmpy)
1.288x10^5 milliinches/(A-cm-year)	milliinches/year (mpy)

3.4.6.3.3 Minimize option

Unfortunately, results may be different from what is expected for two reasons:
1) The linear parts of the plot are not recorded.
2) The potential scan range is too large and an additional electrochemical reaction appears that does not fit the Stern-Geary model.
In these cases, it is possible to reduce the error between the model $I_{calc,i}$ and the measured data $I_{mes,i}$ in minimizing the next value:

$$\chi^2 = \frac{1}{N}\sqrt{\sum_{i=1}^{N}(I_{mes,i} - I_{calc,i})^2}$$

This is obtained in clicking on the **Minimize** button. The Nelder and Mead Simplex method (ref [2]) was used to minimize the χ^2 value. Keep the button pressed (<Enter> or <Alt+M>

keys) until the Stern and Geary parameters E_{corr}, I_{corr}, β_a and β_c have stabilized. Then a "theoretical" Tafel graph is displayed, this graph is displayed in agreement with parameters obtained with minimize button.

Note that the Simplex method may not succeed if the initial values are too much different from the minimum ones (it may fall into a local minimum of χ^2 (E_{corr}, I_{corr}, β_a, β_c)) or if the I(E_{we}) curve is linear around E_{corr}. In that case the following message will be displayed:

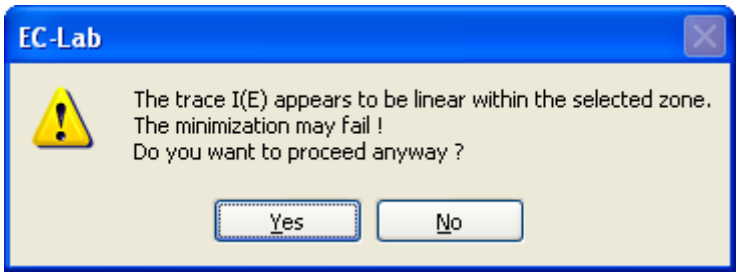

EC-Lab
The trace I(E) appears to be linear within the selected zone.
The minimization may fail !
Do you want to proceed anyway ?
Yes
No

Fig. 178: Tafel Fit minimization message.

For this reason, it is possible to enter directly E_{corr}, I_{corr}, β_a and β_c values and then continue the minimization. Unchecking the boxes around E_{corr}, I_{corr}, β_a and β_c will remove the corresponding value from the minimization. And at any time, one can restart the calculus from the linear fits by clicking on the **Calculate** button.

Reference:

[2] Press W.H., Teukolsky S.A., Vetterling W.T., Flannery B.P., Numerical Recipes in C, second edition, Cambridge University Press, section 10.4, 408-412, 1999

3.4.6.4 Constant Amplitude Sinusoidal microPolarization fit (CASP fit)

The relationship describing the potential modulation *vs.* the sinus of the frequency is given by:

$$E - E_{corr} = \delta E \sin(2\pi f_s t)$$

Then, by applying a Fourier Transform to the former relationship, the resulting current can be described by the following equation [3-4]:

$$I(t) = \delta I_0 + \delta I_1 \sin(\omega t) + \delta I_2 \cos(2\omega t) + \delta I_3 \sin(3\omega t) + \ldots$$

where the fundamental is δI_1 and the two first harmonics are δI_2; δI_3 respectively:

$$\delta I_1 = I_{corr}\left((b_a + b_c)\delta E + \frac{{b_a}^3 + {b_c}^3}{8}\delta E^3 + \frac{{b_a}^5 + {b_c}^5}{8}\delta E^5 + \ldots \right)$$

$$\delta I_2 = I_{corr}\left(\frac{{b_a}^2 - {b_c}^2}{4}\delta E^2 + \frac{{b_a}^4 + {b_c}^4}{48}\delta E^4 + \ldots \right)$$

$$\delta I_3 = I_{corr}\left(\frac{{b_a}^3 - {b_c}^3}{24}\delta E^3 + \frac{{b_a}^5 + {b_c}^5}{384}\delta E^5 + \ldots \right)$$

It is assumed that the harmonics superior to 3 are not significant, so they are neglected in the calculation of I_{corr} β_a and β_c. To validate the fit, δI_1, δI_2 and δI_3 are given in the window. His method yields to valid result if δI_1 is positive, δI_2 is positive or equal to 0 and δI_3 is negative.

The corrosion current is then:

$$I_{corr} = \frac{1}{4\sqrt{3}} \frac{(\delta I_1 + 3\delta I_3)^2}{\sqrt{-\delta I_2^2 - 2\delta I_3(\delta I_1 + 3\delta I_3)}}$$

$$b_a = \frac{2}{\delta E} \frac{\sqrt{3}\sqrt{-\delta I_2^2 - 2\delta I_3(\delta I_1 + 3\delta I_3)} - \delta I_2}{\delta I_1 + 3\delta I_3}$$

$$b_c = \frac{2}{\delta E} \frac{\sqrt{3}\sqrt{-\delta I_2^2 - 2\delta I_3(\delta I_1 + 3\delta I_3)} + \delta I_2}{\delta I_1 + 3\delta I_3}$$

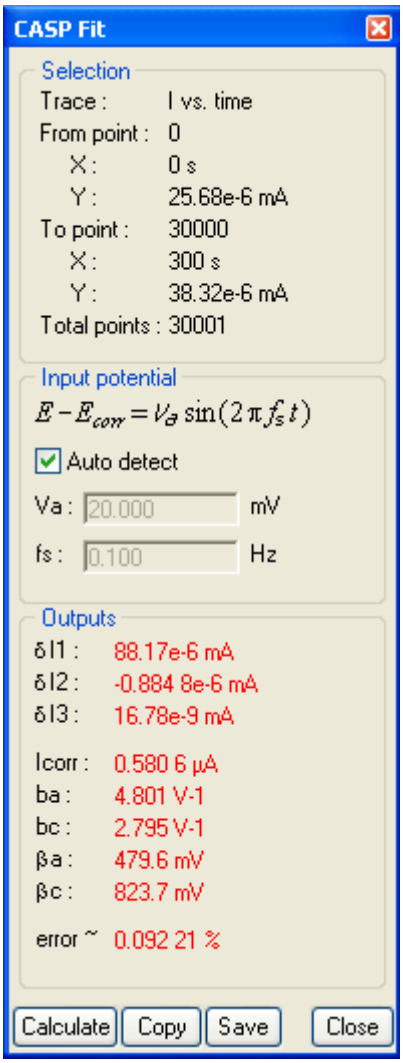


Fig. 179: CASP Fit window.

[3] L. Mészaros, G. Mészaros, B. Lengyel, J. Electrochem. Soc. 141, 8, (1994)
[4] J.-P. Diard, B. Le Gorrec, C. Montella, Comments, J. Electrochem. Soc. 142, 3612, (1995)

This fit is performed with the equation described previously in the Corr. Sim. tool. The amplitude and the frequency sinusoidal excitation applied to the sample can be set manually or automatically as input parameters in the second block of the window.
Note that this analysis is automatically launched after a CASP measurement.

3.4.6.5 Variable Amplitude Sinusoidal microPolarization fit (VASP fit)

In non-linear EIS, the amplitude of the AC voltage exciting signal is higher than in **CASP** technique so the non-linear terms of the Taylor series are significant [5-6]. Then this yields to the following relationship:

$$\frac{1}{R_p} = I_{corr} \sum_{k=0}^{K} \frac{\left(b_a^{2k+1} + b_c^{2k+1} \right) \delta E^{2k}}{2^{2k} k! (k+1)!}$$

"VASP Fit" allows user to fit data from VASP measurements. The ouptut parameters can be given as β or b constant.
The χ^2 is defined by the following equation:

$$\chi^2 = \frac{1}{N} \sqrt{\sum_{i=1}^{N} (X_{mes,i} - X_{calc,i})^2}$$

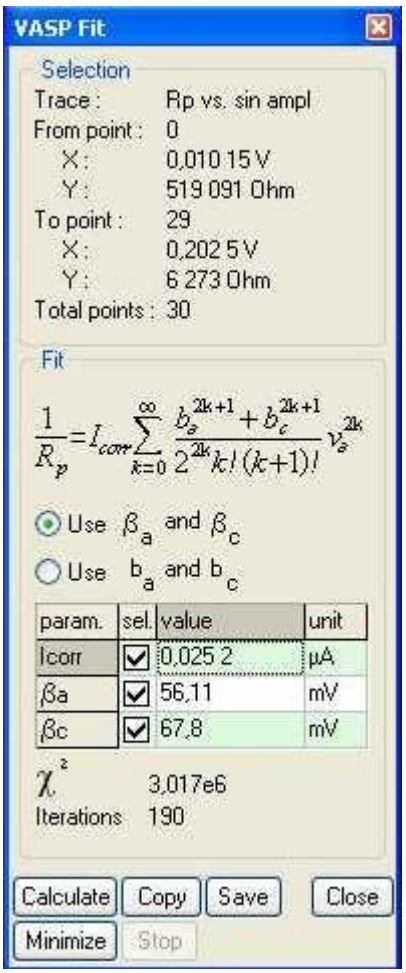


Fig. 180: VASP Fit window.

[5] K. Darowicki, Corrosion Science, Vol. 37, n°6, 913-925 (1995)
[6] J.-P. Diard, B. Le Gorrec, C. Montella, Comments, Corrosion Science, 40, 495 (1998)

3.4.6.6 Electrochemical Noise Analysis

The study of corrosion phenomena by electrochemical noise involves the analysis of random current or potential fluctuations. To study these fluctuations the tool Electrochemical Noise Analysis was introduced into EC-Lab® in the version 10.00.
Electrochemical noise method requires three electrodes to establish a parameter known as the noise resistance R_n. Two of these are working electrodes and current is measured between them at regular intervals. Fluctuations in current and potential are called current and potential noise.
Three methods are available to calculate the electrochemical noise:

- **Standard deviation**. With the two standard deviation values (current and potential) it is possible to apply the Ohm's law relationship and to obtain the parameter (R_n): $R_n = \frac{\sigma_{Ewe}}{\sigma_I}$ with σ_{Ewe}.and σ_I obtained with the formula $\sigma_x = \sqrt{\frac{1}{N-1}\sum_{i=0}^{N-1}(x-\bar{x})^2}$ where $\bar{x} = x$ is the average.

- **PSD with DFT**. It is also possible to calculate the standard deviation from the Power Spectral Density (PSD), indeed according to the Parseval theorem it is possible to link variance σ_x and Power Spectral Density of the x variable $P_{xx}(f)$: $\sigma_x^2 = \int_{-\infty}^{\infty} P_{xx}(f)\mathrm{d}f$.
Note that $P_{xx}(f) = X^2(f)$ where X(*f*) is the Fourier transform of x(*t*).

- **PSD with MEM**. The Maximum Entropy Method (MEM) is an estimation of the PSD suggested by information theory. Calculation of the PSD can be done with the following relationship:

$$P_{xx}(f) = \left| \frac{\Delta t \sigma_u}{1 + \sum_{k=1}^{p} a_k \exp(-2i\pi f \Delta t)} \right|$$

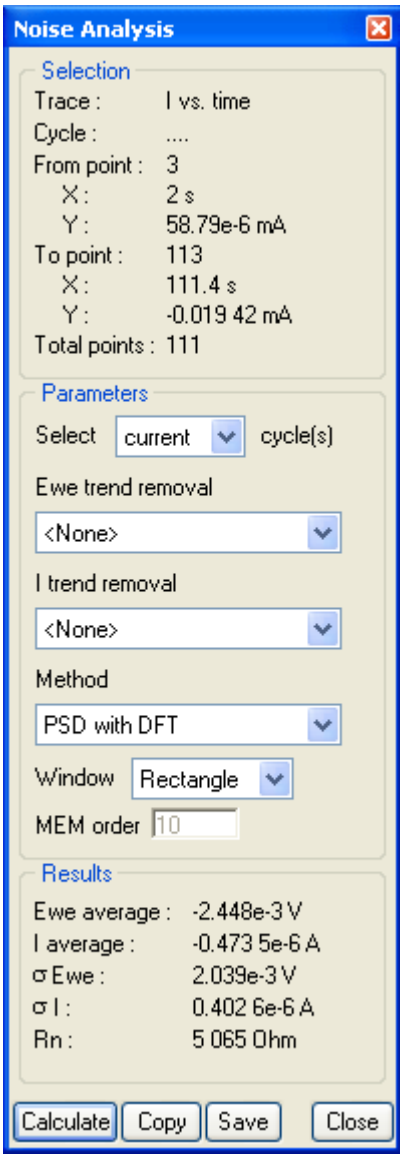


Fig. 181: Electrochemical Noise Analysis window.

In the Parameters part of the window, two choices are available:

- doing the analysis on the cycle displayed on the graph selecting "**Current cycle(s)**",
- doing the analysis on all the cycles selecting "**All cycle(s)**". In this case, the analysis will be performed in all the cycles in a sequential way; the result of each cycle will be saved automatically.

Before to perform the analysis it is possible to remove the trend of the signal (potential and current) by using a **linear fit** or second order **polynomial fit**.
A description of the analysis windows that can be used is detailed in the section Fourier transform 3.4.1.7 page 90.
Example of electrochemical Noise Analysis is given in Fig. 182.

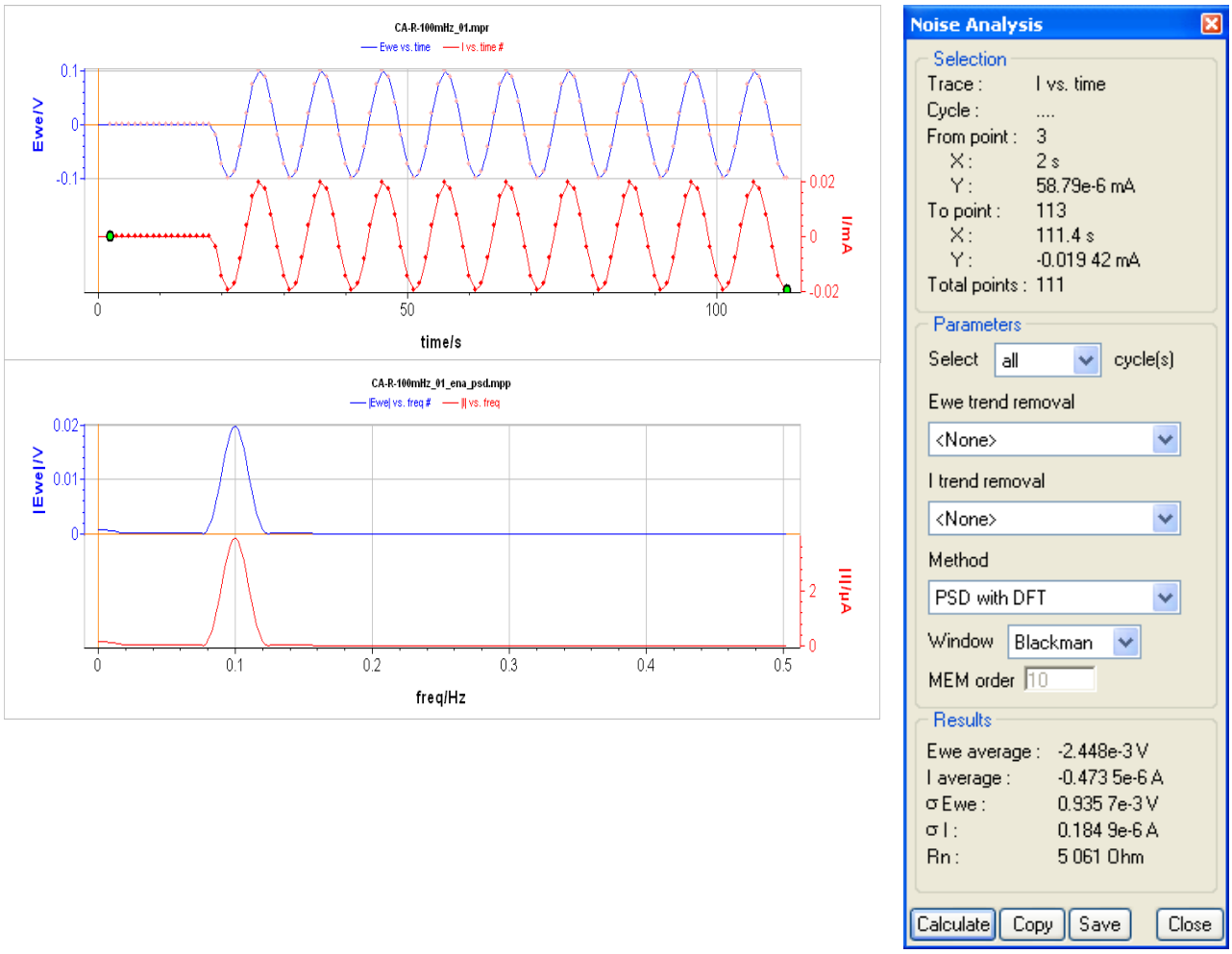


Fig. 182: Electrochemical Noise Analysis on system with a 100 mHz electrochemical noise.

References:

- Bertocci, U., Frydman, J., Gabrielli, C., Huet, F., and Keddam, M., Journal of. Electrochemical Society, 145 (1998), 2780–2786.
- Mansfeld, F., Sun, Z., and Hsu, C. H., Electrochim. Acta, 46 (2001), 3651–3664.
- Lee, C.C. and Mansfeld, F., Corrosion Science, 40 issue 6 (1998), 959-962.

3.4.6.7 Other corrosion processes

Two additional processes are available with the corrosion techniques: polarization resistance and multi-pitting statistics. They are both described in the section below.

3.5 Data and file processing

The structure of the raw files (.mpr) is defined to store all variables of interest and also be as compact as possible (with no variable redundancy).
Nevertheless other variables obtained from the raw file may be of interest. For example, in potentiostatic mode, the instrument acts as a coulometer that performs charge recordings at periodic interval in charge or time. In practice it is more usual to display the current. Thus in such a case, data processing proposes calculating a charge increments between two recordings. From battery experiments several variables are of interest such as resistance. They can be extracted from raw data files in a compacted file.

3.5.1 Data processing

General variables can be processed with the process data function. From the EC-Lab® menu choose the **Analysis** menu and for each of the analysis category, a list of processing functions can be applied to raw .mpr data files. Hereafter are summarized all the processes:

- General Process data window
- Capacity and energy per cycle and sequence
- Summary per protocol and cycle
- Constant power protocol summary
- Polarization resistance
- Multi-pitting statistics.

All these functions are available off-line after the experiment. They create new binary files (.mpp) based on .mpr files with additional or removed variables. These files can be created during the experiment at a given time or after.

3.5.1.1 Process window

Select **Analysis, Batteries, Process Data** to load the processing window

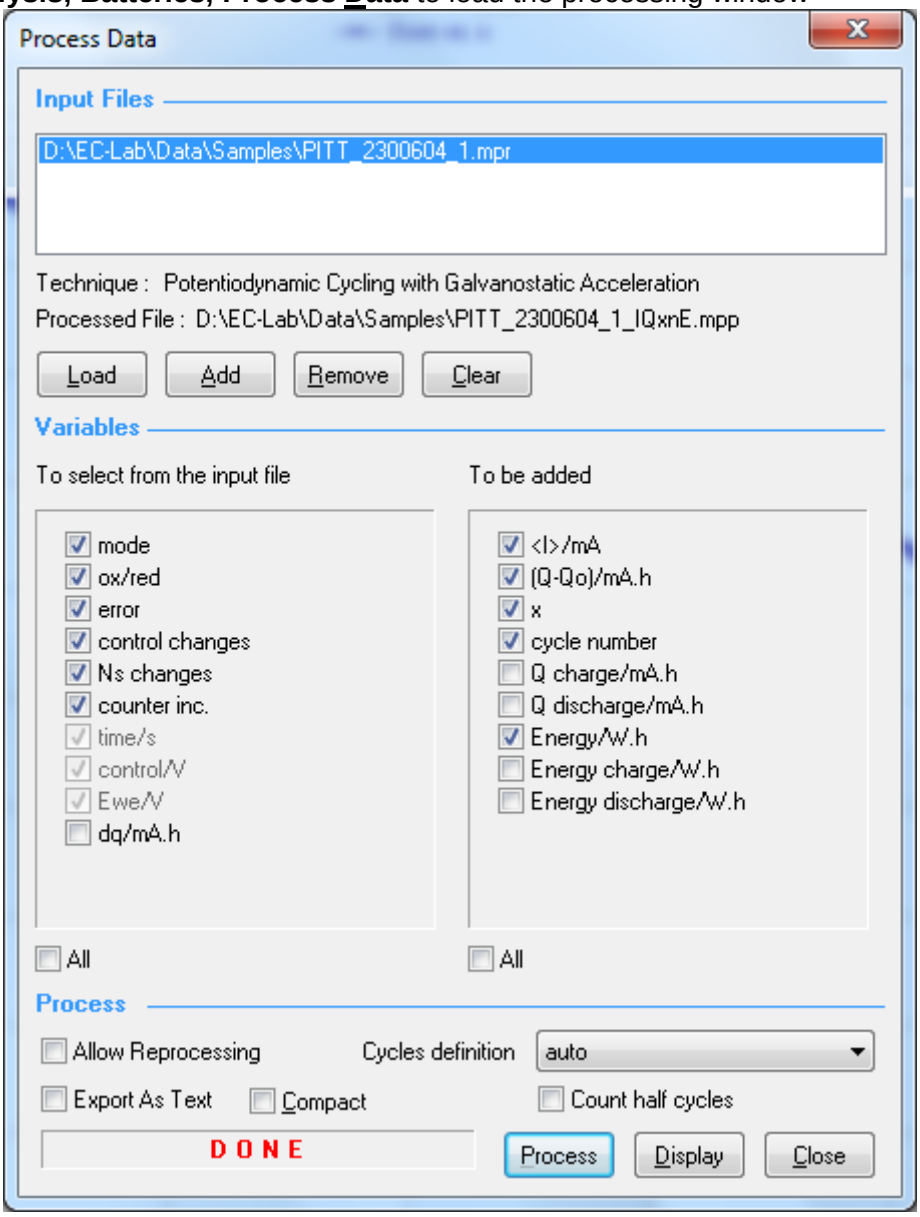


Fig. 183: PCGA Process window

This window is separated in 3 parts:

- in the first part “Input File” on the top of the window, the user will add the raw data files to process. Click on the **Load** button to load a raw data file (in our example a PCGA file).
- The second part “Variables”, is dedicated to the variable selection generated the processed file. The left section is for the variable selection (from the native raw file) and the right section for those to be added to the processed file (calculated into either the firmware such as <I>, ($Q-Q_0$) or in the computer as processed variables such as Q and energy in this case.
- The bottom section is for additional options in the process. It is possible to:
    - Allow reprocessing to be able to process again a mpp file
    - Export as text a batch of data files
    - Define the cycle as Auto / loop increment / every charge discharge alternance,
    - Compact file for PCGA to add the dQ variable,
    - Keep only values at the end of every Eoc period or I on period for GCPL
    - Count half cycles

Select the variables you want to add and click on the **Process** button. This will create the processed file with the same name as the raw file, but with the addition of letters corresponding to the selected new variables and the .mpp extension instead of .mpr.

3.5.1.2 Additional processing options

At the user’s convenience, the processed file can contain only a part of the native variables of the raw file. In that case the processed file will not be processable again. But for a later process of the processed file, the “**Allow Reprocessing**” box must be ticked on. This option will automatically select all the variables of the native raw file.

An “**Export as text**” option as been added in this window to automatically generate a text file processed file (*.mpt) that may be used in other software.

Different ways exist to define cycles in the processed file in order to plot Q and energy during the charge and discharge steps. The cycle for the process can be defined **automatically** or **every loop increment** or every **charge/discharge alternation**.

For the battery applications, specific process options “**Keep only values at the end of every OC period, I on period**” and “**Compact**” are available for the compacting process (for more details see the description below).

A “**Count half cycle**” process is available to separate half cycles especially for discharge discharge measurements in battery testing.

Additionally, a process is also available for QCM experiment and especially for the determination of Mass variations. Using the auxiliary inputs of our instruments and a good setting to record the frequency changes, the software is able to process the mass variations. This feature is described in details in the application note #13.

3.5.1.3 The derivative process

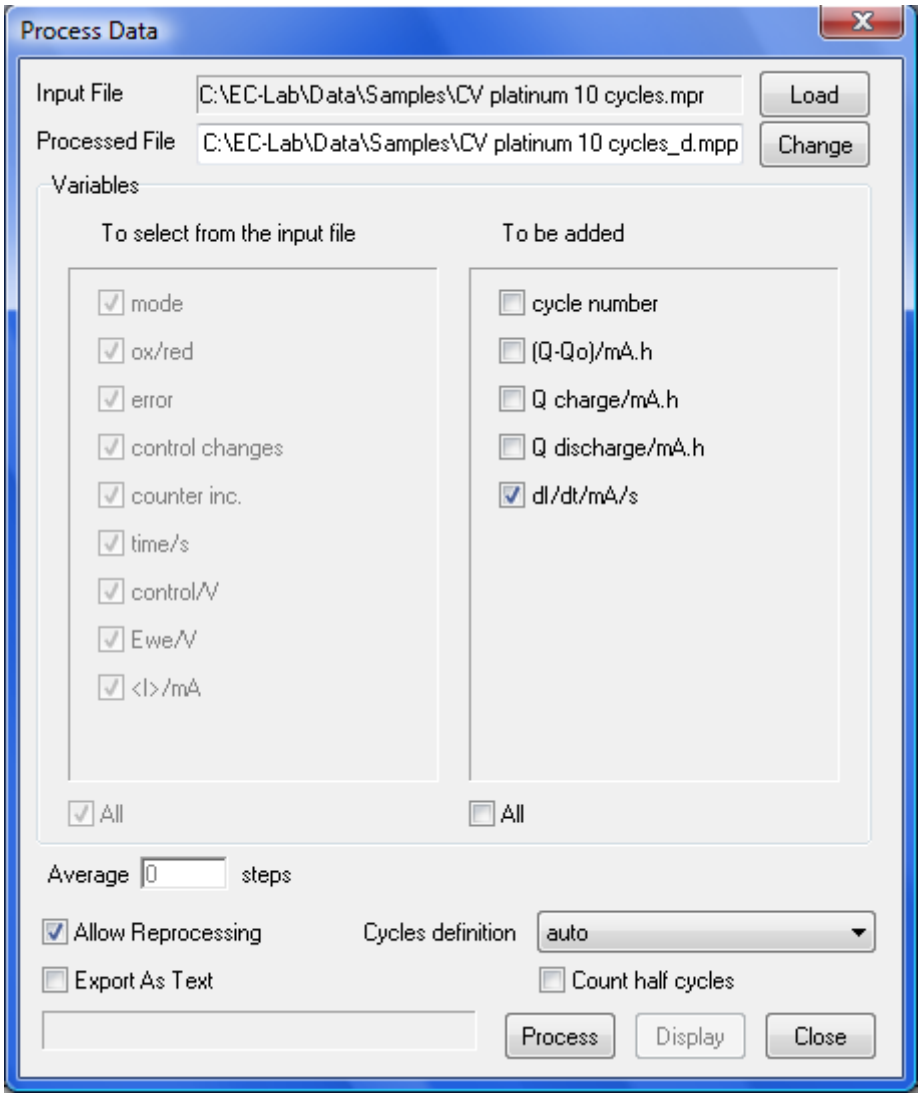


Fig. 184: Cyclic voltammetry processing window.

For techniques resulting in a current measurement (when the potential is controlled), the user can process the data file to create a new variable dI/dt, the derivative of the current versus time. Click on Display to automatically display the processed variable on the graph. The example below shows the Current derivative curve plotted versus the potential overlaid with the native cyclic voltammetry.

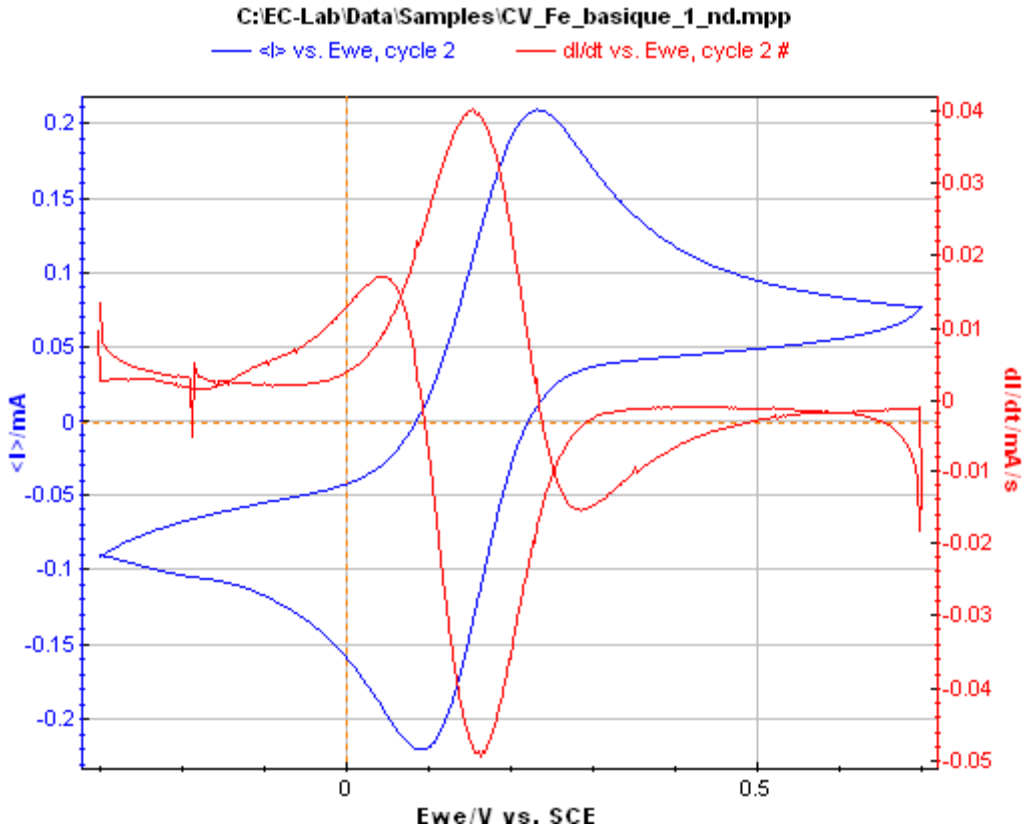


Fig. 185: Overlay Cyclic voltammetry with derivative curve.

All the graphic tools and fits can be applied to the derivative curve.

3.5.1.4 The compact process

The **Compact** function or "**Keep only values at the end of every OC period, I on period**" function can be used in GCPL and PCGA protocols. In the GCPL protocol, this function results in the determination of the apparent resistance "**Ri**" of the material studied (see the next section about GCPL). In the PCGA protocol, this function results in the determination of one average value of the variables for each potential step. Selecting **Compact** compresses the data resulting from the raw data file. All the points of each potential step are replaced by their average (current, potential, x or Q) taken at the end of the potential step. One consequence is an important decrease in the number of points in the compacted file compared to the raw file. The figure below shows the effect of the compact function on the current plot.

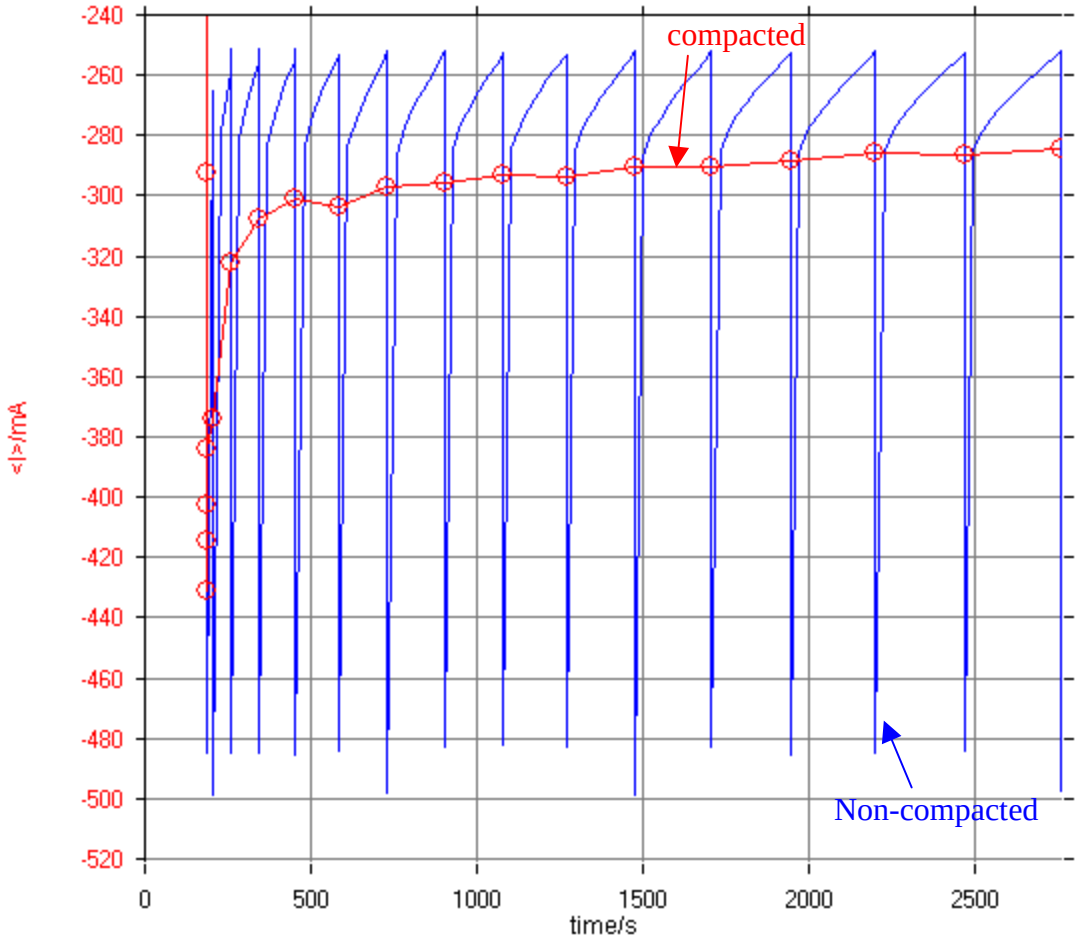


Fig. 186: Overlaid compacted and non-compacted current curves.

The variables that can be obtained from compacted files appear when the boxes at the bottom of the process window are ticked: "**keep only values at the end of every open circuit period** and/or **I on period**.

3.5.1.5 Capacity and energy per cycle and sequence

Capacity and energy per Cycle and sequence... Calculates the capacity, energy and capacitance per cycle for the Galvanostatic Cycling with Potential Limitation (GCPL), Chronoamperometry / Chronocoulometry (Chrono I/Q), Cyclic Voltammetry (CV) and Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA) files. The values are calculated for both the charge and the discharge. The generated file is a compacted file. The user can define the frequency the data points are recorded (every sequence or every cycle). He can set the cycle definition to be done automatically or every loop or every charge/discharge alternance.

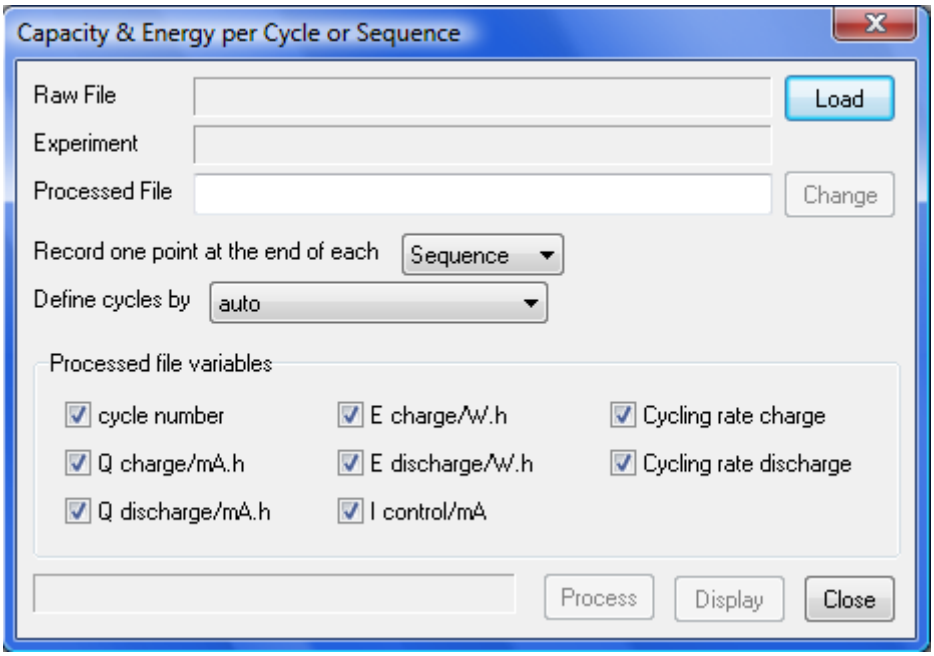


Fig. 187: Capacity and energy per cycle and sequence processing window.

The result of the calculation is a compacted processed file that contains several columns depending on the selected variables. The values can be processed as densities using the electrode surface area or the characteristic mass.

3.5.1.6 Summary per protocol and cycle

This process allows the user to analyze CV, CA, CP, GCPL, GCPL2, GCPL3 and PCGA linked experiments in calculating Q_{anodic}, $Q_{cathodic}$ and X_{min} and X_{max} (X being I_{anodic}, $I_{cathodic}$...) for each cycle and linked experiment loop. Select this tool in the General electrochemistry analysis:

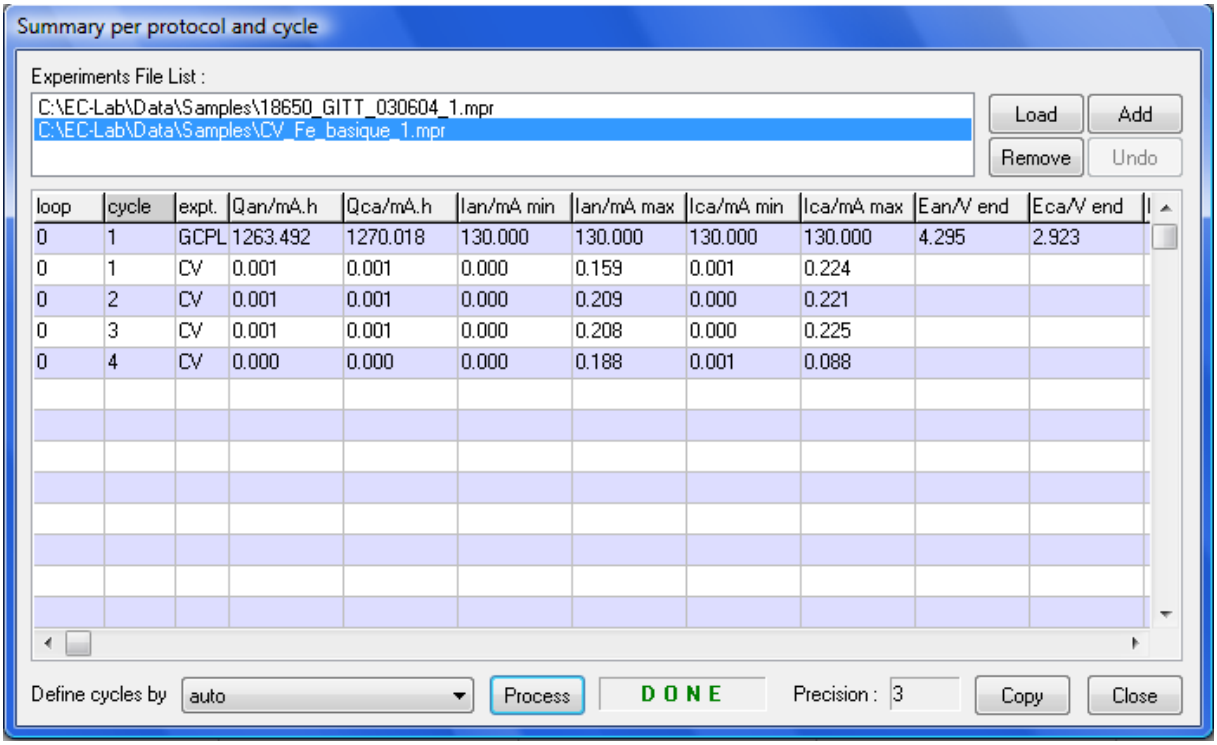

Summary per protocol and cycle
Experiments File List :
C:\EC-Lab\Data\Samples\18650_GITT_030604_1.mpr
C:\EC-Lab\Data\Samples\CV_Fe_basique_1.mpr
Load
Add
Remove
Undo
loop cycle expt. Qan/mA.h Qca/mA.h Ian/mA min Ian/mA max Ica/mA min Ica/mA max Ean/V end Eca/V end
0 1 GCPL 1263.492 1270.018 130.000 130.000 130.000 130.000 4.295 2.923
0 1 CV 0.001 0.001 0.000 0.159 0.001 0.224
0 2 CV 0.001 0.001 0.000 0.209 0.000 0.221
0 3 CV 0.001 0.001 0.000 0.208 0.000 0.225
0 4 CV 0.000 0.000 0.000 0.188 0.001 0.088
Define cycles by
auto
Process
DONE
Precision :
3
Copy
Close

Fig. 188: Summary per protocol window.

Then, select the raw data files that correspond to two experiments, with the **Load** (**Add**, **Remove** and **Undo**) buttons. In the example above:

- 18650_GITT_030604.mpr.mpr
- CV_Fe_basique_1.mpr

correspond to a GCPL and a CV run with cycles in each technique.

Click the **Process** button to start the calculation. This will create one processed file per raw file that contains the results (in the example: 18650_GITT_030604.mpr.mpp, CV_Fe_basique_1_cnQ.mpp) and displays the results in the Linked experiment window grid.

Notice that the linked experiment loops and the electrochemical cycles are both displayed and that the Summary per protocol and cycle window can be resized to full screen to display more values in the grid.

The grid can be copied to the clipboard (and pasted into a spreadsheet...) with the **Copy** button.

If one requires more accuracy, it is possible to increase the grid precision (up to 10 digits) by the following operations:

- change the **Precision** value,
- click again on the **Process** button.

Note that if the processed files are already calculated, this is not necessary to rebuild them (respond **Cancel** when the program asks you to rewrite them). Then the grid values will be reloaded from the existing processed files with the new precision.

The processed files are not deleted after the process and can be displayed in an EC-Lab® graph, or exported one by one into ASCII format.

3.5.1.7 Constant power protocol summary

A process called "Constant Power technique summary" has been especially designed for Ragone plot representation. It is associated with the CPW technique in battery applications. To use this data process, click on "process" in the graphic window or choose "Batteries\Constant Power Protocol summary" in the **Analysis** menu. Then the following processing window will be displayed:

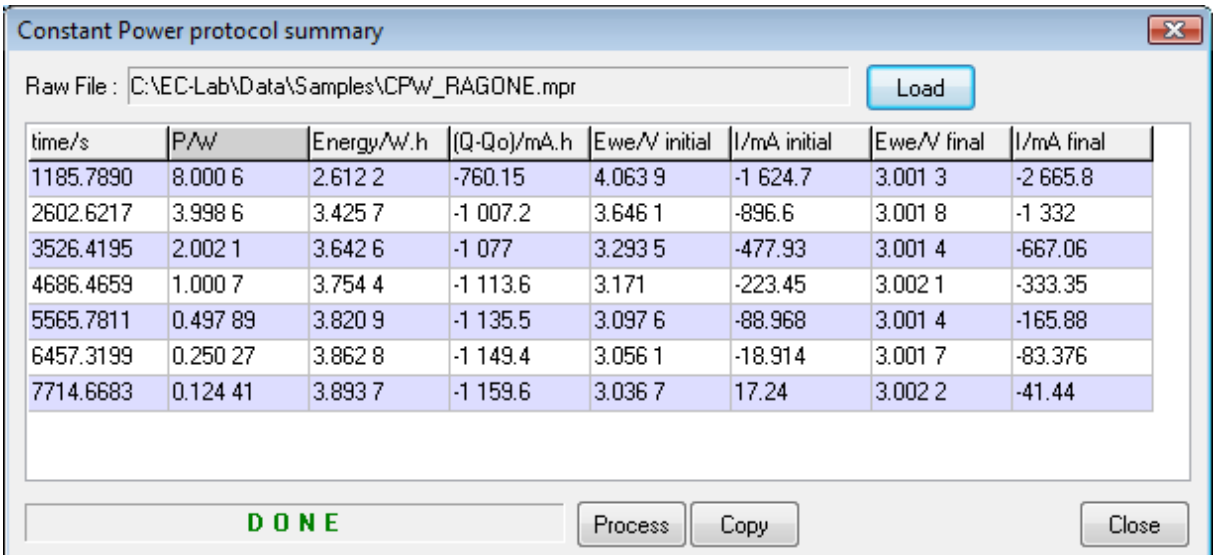


Fig. 189: CPW process window.

This process window is made of a table containing the characteristic variables of each power step, such as the time, the energy and charge of the end of the step, the working electrode potential and the current that crossed the cell at the beginning and the end of the step. The "Copy" tab allows the user to paste the values of the table in a graphic software in order to have a Ragone plot (see figure below):

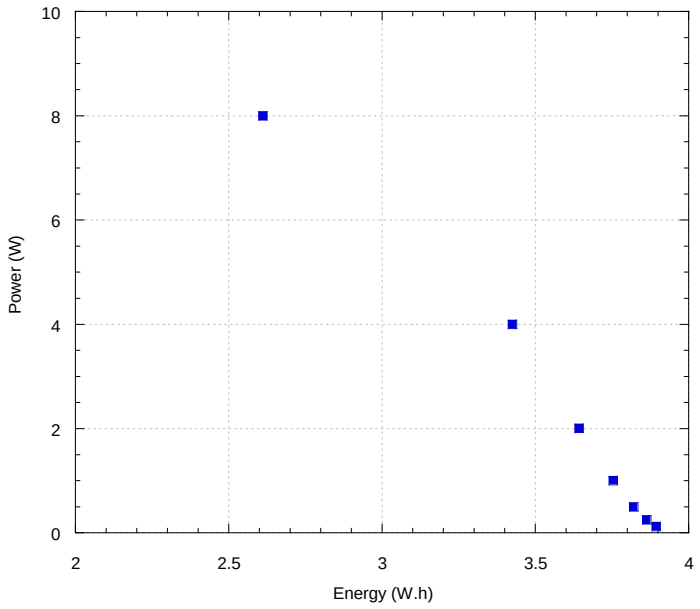


Fig. 190: Ragone plot for a Li-ion cell (1.35 A.h).

3.5.1.8 Polarization resistance

Polarization Resistance... determines the R_p and I_{corr} values from a Polarization Resistance files. Select **Analysis/Corrosion/Polarization Resistance** to load the following window.
Click on the **Load...** button to select a polarization resistance file. Then a summary of the parameters will be displayed into the settings frame. Note that it is possible to modify the electrode surface area value (for R_p in $\Omega.cm^2$ calculus) here.

.

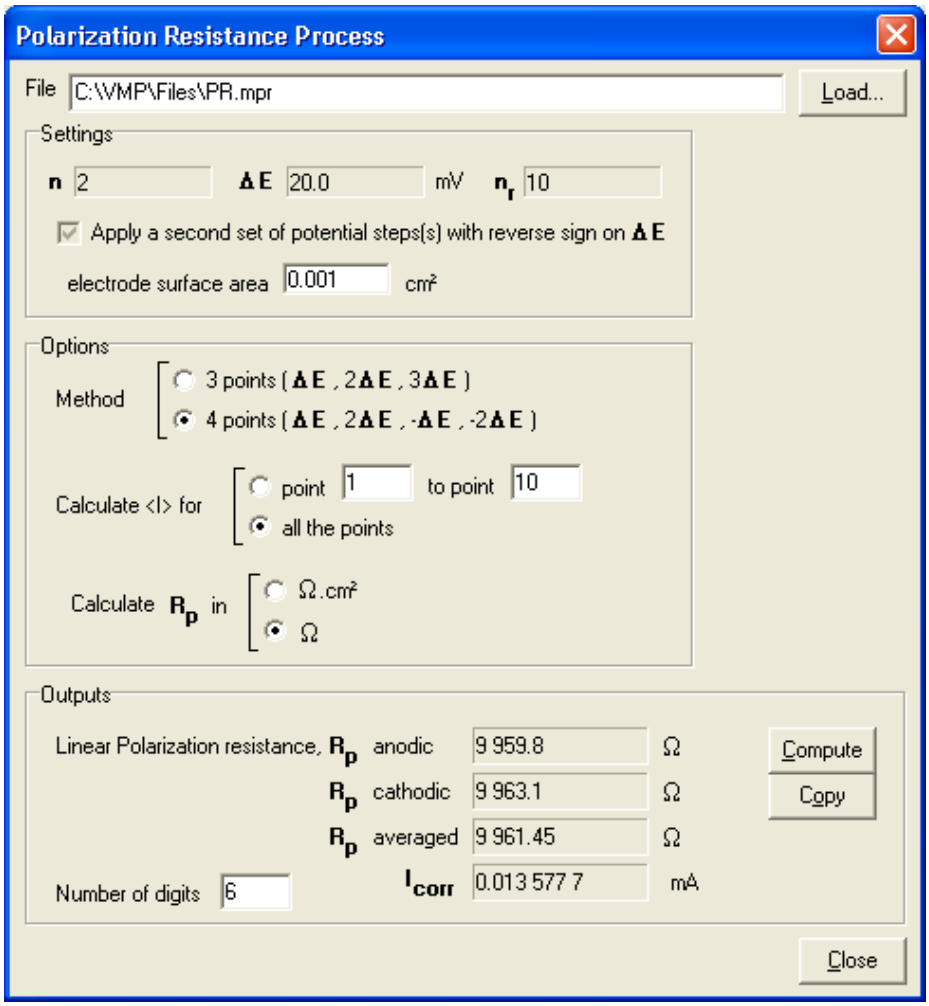


Fig. 191: Polarization Resistance process.

Then according to the experiment type, it is possible to select the 4 points or the 3 points methods that both correspond to specific settings:

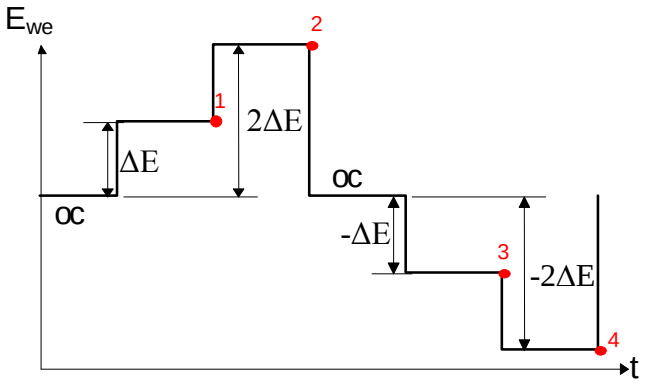


Fig. 192: 4 points method.

(n = 2, reverse steps)

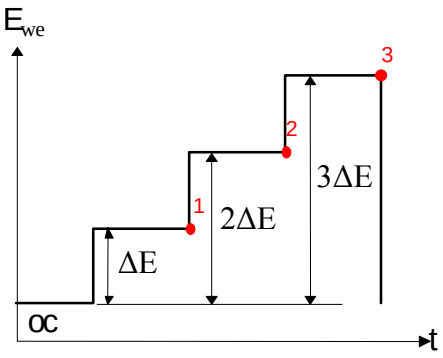


Fig. 193: 3 points method.

(n = 3, do not reverse steps)

The 4 points method gives more accuracy, so it is proposed by default. Nevertheless, it is not always possible to make a reduction after an oxidation, so then chose the 3 points method.

Note: one can perform more than the 4 points and 3 points method with the Polarization Resistance technique, but the process here accepts only these two.

If several points have been recorded per potential steps (n_r > 1), it is possible to exclude some points for the calculus. For example, selecting Calculate <I> for point 3 to 10 will exclude the first two points.

Chose the R_p unit ($\Omega.cm^2$ or Ω) and click on **Compute** to calculate the next values:

$$R_{p_{anodic}} = \frac{e_2 - e_1}{i_2 - i_1}, \ldots R_{p_{cathodic}} = \frac{e_4 - e_3}{i_4 - i_3} \ldots \text{ and } R_{p_{averaged}} = \frac{R_{p_{anodic}} + R_{p_{cathodic}}}{2}$$

3 points method: $I_{corr} = \frac{i_1}{\sqrt{\left|4r_2 - 3r_1^2\right|}}$ with $r_1 = \frac{i_2}{i_1}$, and $r_2 = \frac{i_3}{i_1}$

4 points method: $I_{corr} = \frac{i_1 i_3}{\sqrt{\left|i_2 i_4 - 4 i_1 i_3\right|}}$ with (e_1,i_1) being the potential and the average current (without excluded points) on the potential step ΔE, (e_2,i_2) on $2\Delta E$, (e_3,i_3) on $-\Delta E$ or $3\Delta E$ (according to the selected method) and (e_4,i_4) $-2\Delta E$

Note: if there are several loops (n_c > 0), then the (e_n,i_n) values are averaged on the different loops before the calculus.

3.5.1.9 Multi-pitting statistics

Multi-Pitting Statistics... is a process which can be applied to Multi-Pitting experiment files. It gives the mean value <E> and the mean quadratic deviations σ of the final open circuit potentials (E_{oc}) and pitting potentials (E_p) of a set of electrodes, or of a set of selected files. .

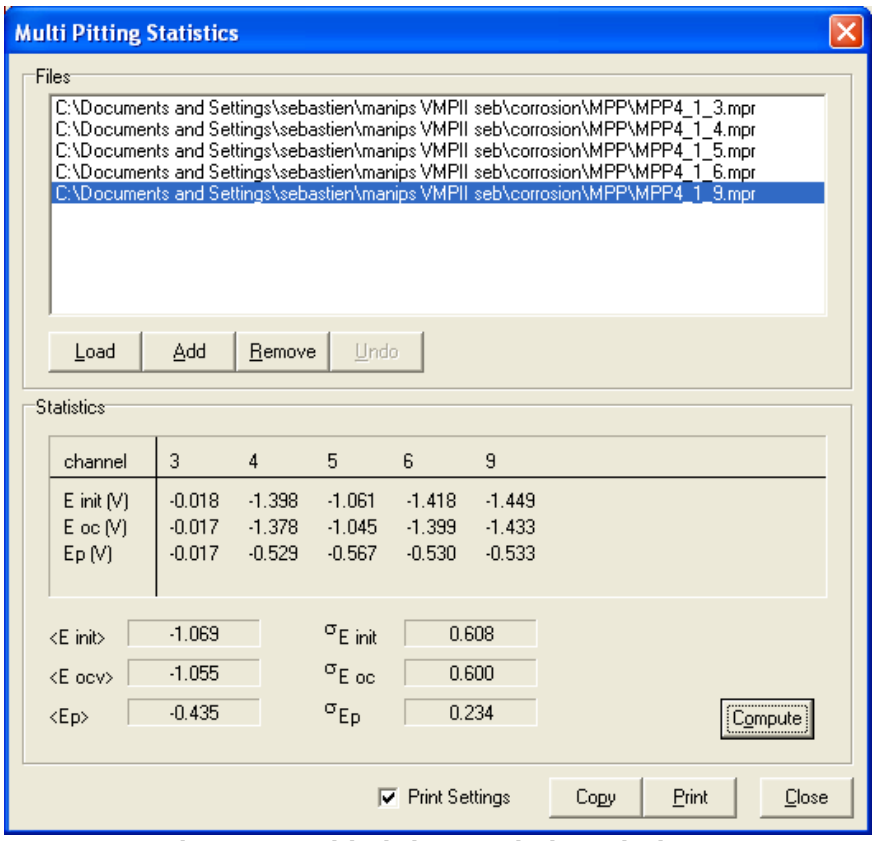


Fig. 194: Multi pitting statistics window.

Note that the E_p value corresponds to the potential measured for I = I_p.

3.5.2 Data File import/export functions

3.5.2.1 ASCII text file creation and exportation

For file exportation to other software (Kaleidagraph, Origin, Excel,...), it is possible to create text files from .mpr and .mpp files. Choose **Tools, Export as Text…** in the EC-Lab® menu bar. This will load the window below.

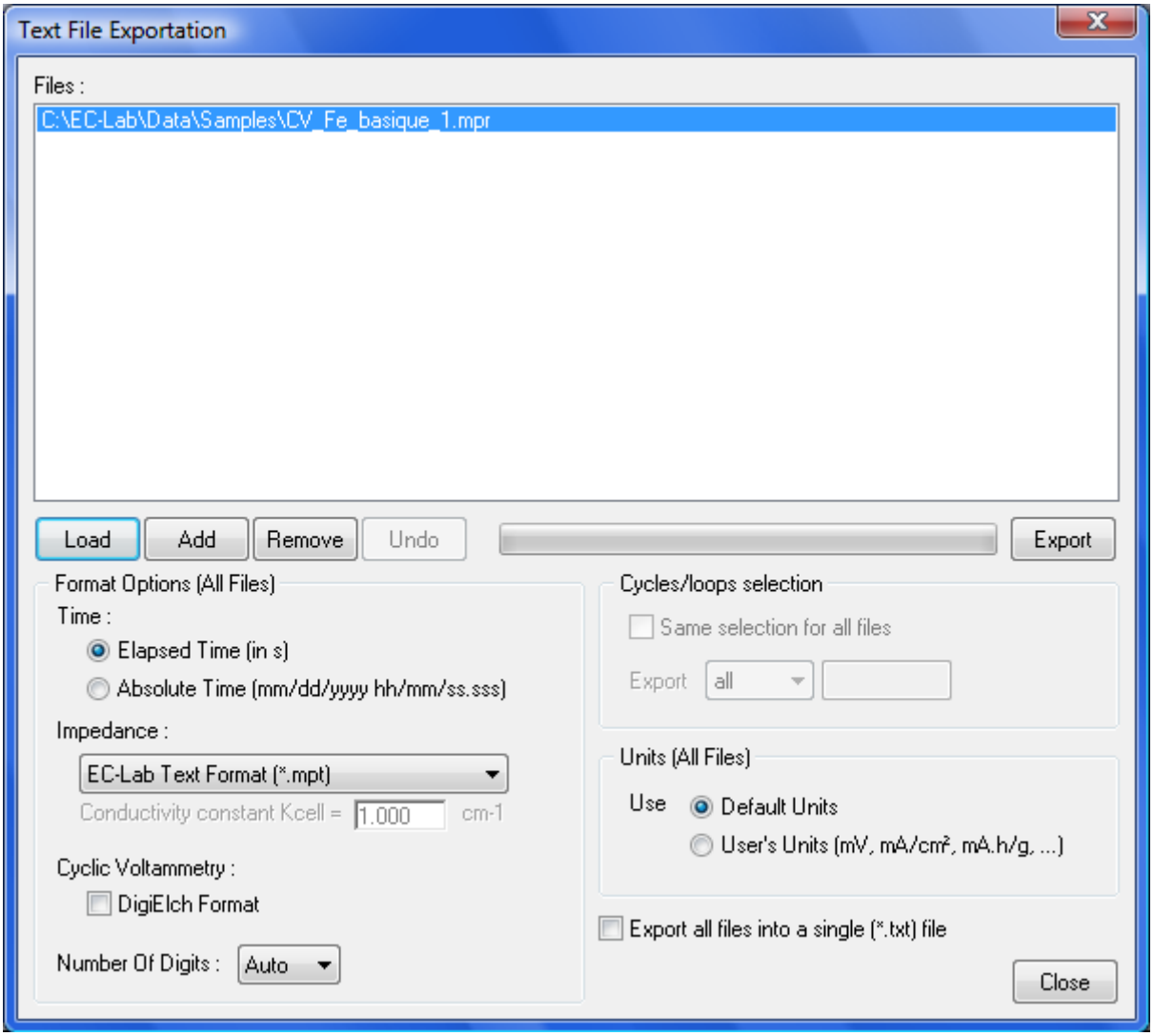


Fig. 195: Text File exportation.

Select one or more files (with the **Load** and **Add** buttons). Note that it is possible to select files from different directories. Click on the **Export** button to export all the selected files into the selected text format. The resulting text file(s) are created in the same folder as the original file and differs only by the **.mpt** extension.

Several text formats can be created by EC-Lab® software depending on the importing software. For time files one can display the relative time from the beginning of the experiment e.g. t = 0 s for the first point (**Elapsed Time (in s)** option, default) or the absolute time in year, month, day, hours, minutes and seconds format (**Absolute Time (mm/dd/yyyy hh/mm.ss.sss** option). For impedance data files, an export text in ZSimpWin or Zview

formats is available and allows to paste directly data into ZSimpWin or Zview software. An export text in Bio-Kine conductivity Ascii file is also available. For cyclic voltammetry files, an export option in DigiElch format is available. A *.use file is created in that case.

While running experiment, it is possible to export files. To do so, the user must check the **Text export** option into the "Cell Characteristics" window before starting the experiment.

Loops / cycles text exportation:
If the selected file contains linked experiments loops or the cycle number variable (processed files only), then one can export specific loops or cycles.

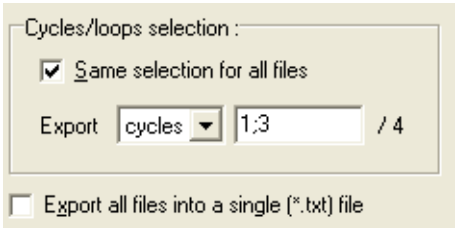


Fig. 196: Loops/cycles text exportation.

Proceed in the same way as with the **Selector**: check **Same selection for all files** if you want to apply the loop/cycle selection to all the selected files. If unchecked, each selected file will have its own loop/cycle selection.Select loop or cycles (if present) with the **Export** box and edit the selection list with the following rules:
- separate each single item by a ';' : <item1>;<item2>;<item3>;...
- use '-' to generate a list of consecutive items : <first item>-<last item>;...
The example above: '1;3' will select the cycles number 1, and 3.

Once the loops or cycles have been selected the text exportation will create one file per loop or cycle selected with the loop or cycle number added to the text file.
Note: the user can copy data in text format. Right click with the mouse and select copy data. The displayed variables will be copied to the clipboard.

Unit selection
On the graphic window, EC-Lab® software is capable of plotting variable density (for example normalized current with mass or surface). These new variables are not stored in the data file and cannot be exported as text. To allow exportation of densities, the user can select the unit. The default one will not include the density and the user's units will include densities. :
Note: A text data file can be generated automatically during the experiment if the box "Text export" is checked in the "Advanced setting" window.

3.5.2.2 ZSimpWin exportation

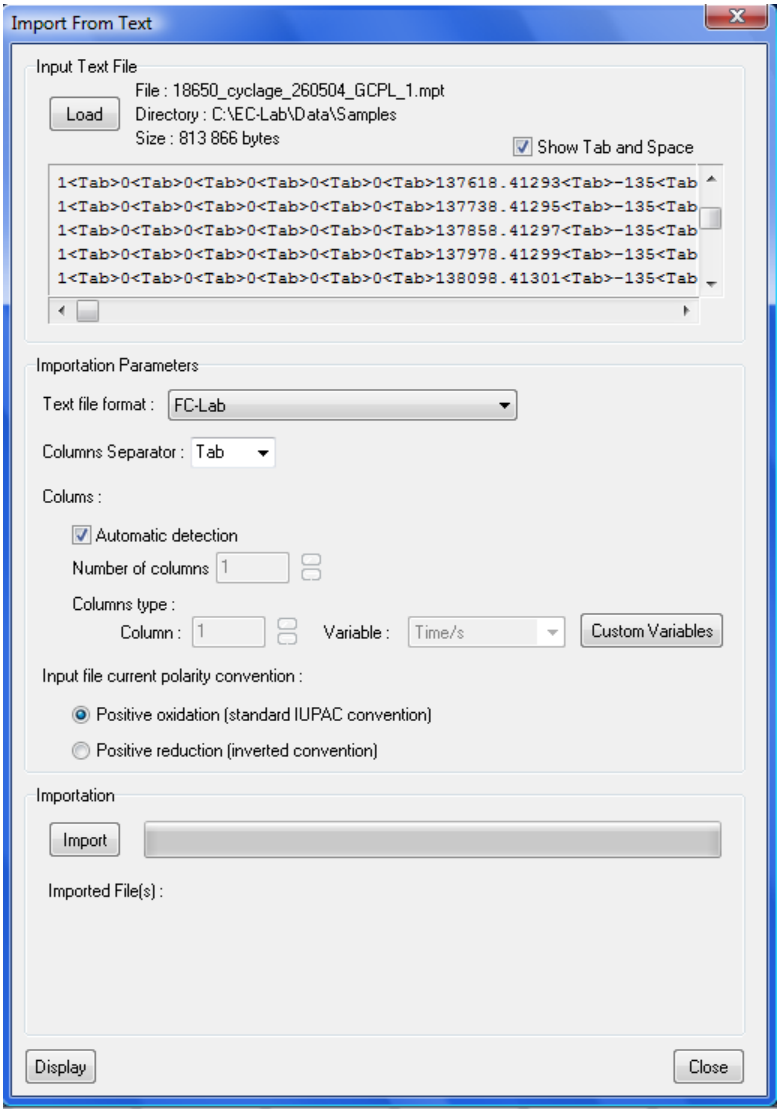
It is possible to export data directly into ZSimpWin through the Clipboard. To proceed, open an impedance data file, right click with the mouse, and select **Copy Z Data (ZSimpWin)**, or click directly on the **Copy Z Data (ZSimpWin)** button in the Edit menu. Then the data points will be copied into the clipboard and can be pasted directly into ZSimpWin.
Warning: For good compatibility, the text file exported into ZSimpWin must contain between 16 and 199 points.

3.5.2.3 ASCII text file importation from other electrochemical software

EC-Lab® software allows the user to load every text file generated by other electrochemical software. All text formats can be loaded directly from the "**Load data file"** function in the **Experiment** menu. If the software recognizes the data file, EC-Lab® will be able to open it

directly. If not the user can import the text file with the "**Import from text**" function in the **Experiment** menu. This can be done either automatically when it is possible (the format is known by the software) or manually with a definition by the user of the number of columns and of each variable.

In the "**Tools**" menu select "**Import from text…**" or click on the import icon to display the following window:



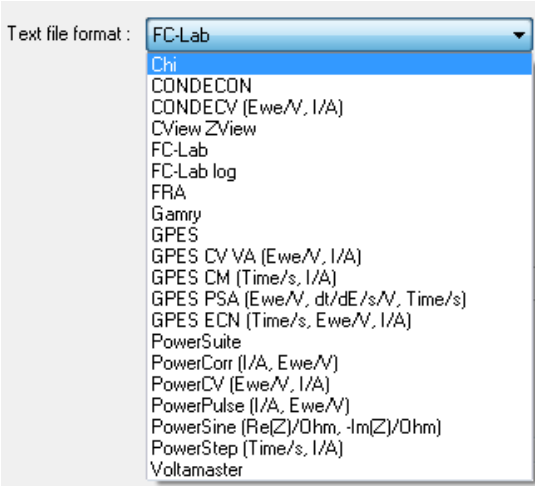


Fig. 197: Text file importation into EC-Lab® and available importation file formats.

To proceed to text file importation, click on the "**Load**" button and select the file to import. Now the file name, directory and size are displayed near the top of the window in the "**Input Text File**" frame.
The second frame defines the parameters for importation. In order to select the good separator, click in the "**Show tab and space**" box to display separators in the file. You can try with an automatic detection. In most of the cases the user will have to use a manual detection while unchecking the box. Then define the number of columns and for each of them select the variable. The user can add his own labels and units to be displayed in the data file and the graphic window.
Then click on the "**Import**" button to import the file into the EC-Lab® .mpr format. The mpr file is created in the same folder as the text file. Several details are displayed when the file is created such as the name, the number of points and the size.
Finally the user can display the .mpr file quickly and easily with the "**Display**" button. Every analysis of EC-Lab® is available with the new generated files.

3.5.2.4 FC-Lab data files importation

FC-Lab® data files can also be imported and analyzed in EC-Lab® using the "**Text file format**" function. The FC-Lab® data file format is particular as all the data files for each technique are in the same file. So EC-Lab® software will separate every file of every technique used in the experiment.

3.6 Reports

A report file can be associated with each EC-Lab® data file to add all kinds of additional information. The data file and the report file have the same name but with different extensions: .mpr for the data file, and .rep for the report file. Note that the report file must be in the same directory as the corresponding data file in order to be recognized.
For instance:
- Data file: *c:\vmp\files\XXXX.mpr*
- Report file: *c:\vmp\files\XXXX.rep*

Reports are called from the Graphic Display window. Right click with the mouse on the graphic window and select "**Report**" to call the report associated with the current data file. If the report does not exist, a message box appears to let the user create a new report:

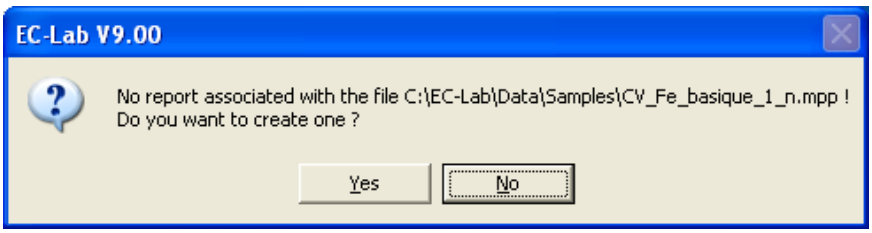


Fig. 198: Message window.

Here is an example of a report. The user can define the project, material and results.

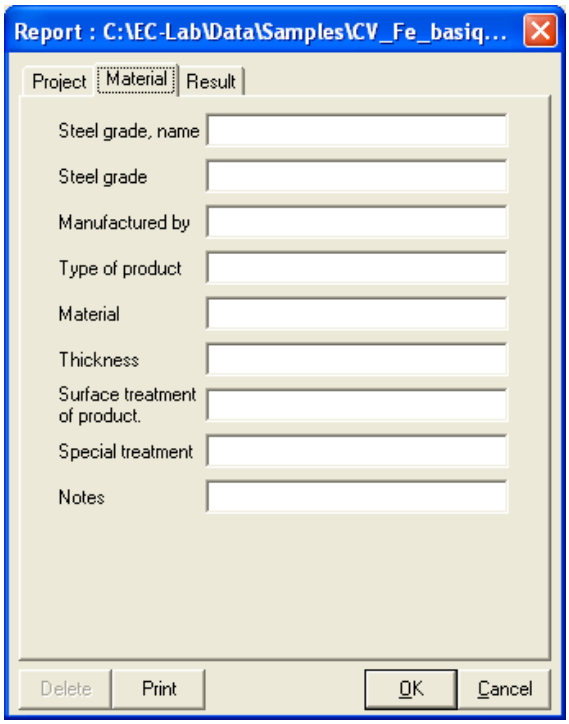


Fig. 199: Report window.

OK saves modifications done to the report.
Cancel discards modifications done to the report.
Delete automatically sends the report to the recycle bin.

Report configuration

The structure of each new report is based on the read-only text file *"DefaultReport.rep*" (in the same directory as the EC-Lab® software), which is given as an example. However, the user can change the sections and keys to customize the report to his needs.
For example the changing of the content of "*DefaultReport.rep*" into:

[Section1]
Info1=
Info2=
[Section2]
Info10=
Info20=

will result in the new report:

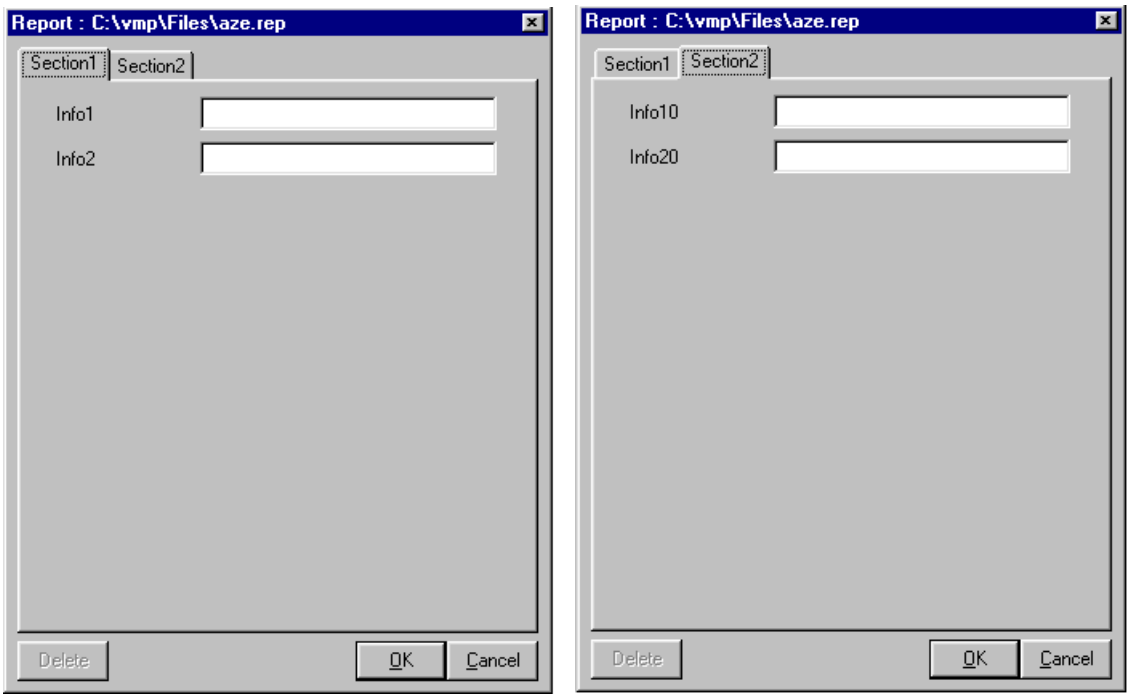


Fig. 200: New Report.

4. Linked experiments

4.1 Description and settings

It is possible to link different protocols within the same run. This allows the user to create and build complex experiments composed up to 20 techniques. When created the linked experiment settings can be saved either as an .mps file or as a "**Custom application**". In the first case the settings can be loaded from the initial folder, and in the second case they appear in the applications and can be reloaded whenever necessary.

Linked experiments can be made using the "**technique builder**" in the technique window. The WAIT and LOOP options have been designed specially for linked experiments.
Building linked experiments is very easy with settings on the right click menu. When the user right clicks on the parameter settings window, the following menu pops up:

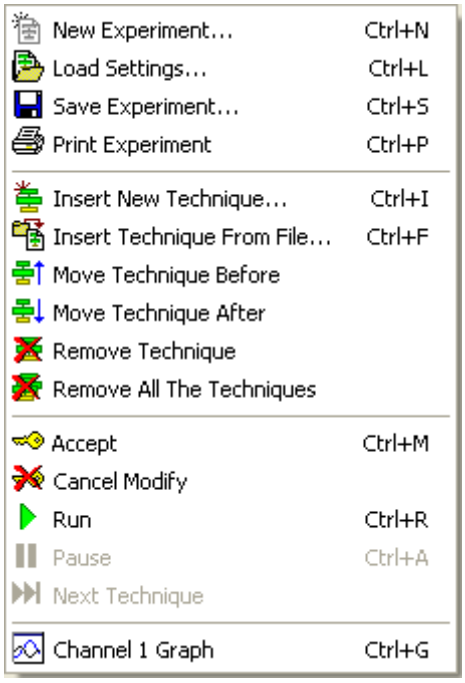


Fig. 201: Mouse right click with the insert and remove options.

The second frame is especially dedicated to linked experiments. The "**Insert New Technique**" function opens the technique selection window and can insert a new technique into the experiment. The user can select where he wants to add the new technique into the settings according to the activated/selected technique (green frame around the technique name) in the parameter settings window at the bottom left corner frame of the technique selection window:

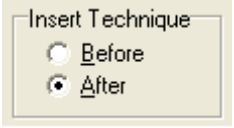


Fig. 202: Insert before/after option of the technique selection window.

If the technique is not in the correct position in the series of experiments, the user can easily move it up or down using the "**Move Technique Before**" and "**Move Technique After**" options respectively.

Note: it is possible with the protocol linker to apply 50 ms OCV period between two protocols (reduced to 0.6 ms if the previous protocol is an OCV). The user has just to activate "**Turn to OCV between protocols**" in the advanced settings window. If this option is not selected the user will not have the ability to select different current ranges for each linked technique.

Note that more than one loop can be added to a linked experiment.

When the user clicks the Run button, the program asks for a file name that will be used for all the linked experiments with the following rules:

experiment file name = user file name + "_" + experiment number + "_" + experiment (short) name + "_" + "channel number" + ".mpr"

For example: the file name "MyFileName", will be used to generate these files:

experiment 1: no file name for the Trigger In option
experiment 2: MyFileName_2_MP_01.mpr
experiment 3: MyFileName_3_WAIT_01.mpr
experiment 4: no file name for the protocol linker loop

Each of these files will store the corresponding data points for all the loops.

Note:

1- It is possible to synchronize linked experiments on several channels.

2- One data file can be created per technique and per loop in a linked technique. In the "Advanced settings" window, tick the box corresponding to "Create one data file per loop". The file name is created as follows:

"Filename" + _ + "technique number in link" + _ "technique name" + _ + "channel number" + _ + "loop#".mpr"

4.2 Applications

4.2.1 Linked experiments with EIS techniques

The following experiment is given as an example of linked experiment. This experiment is composed of OCV, CA, CV, PEIS and Loop techniques.

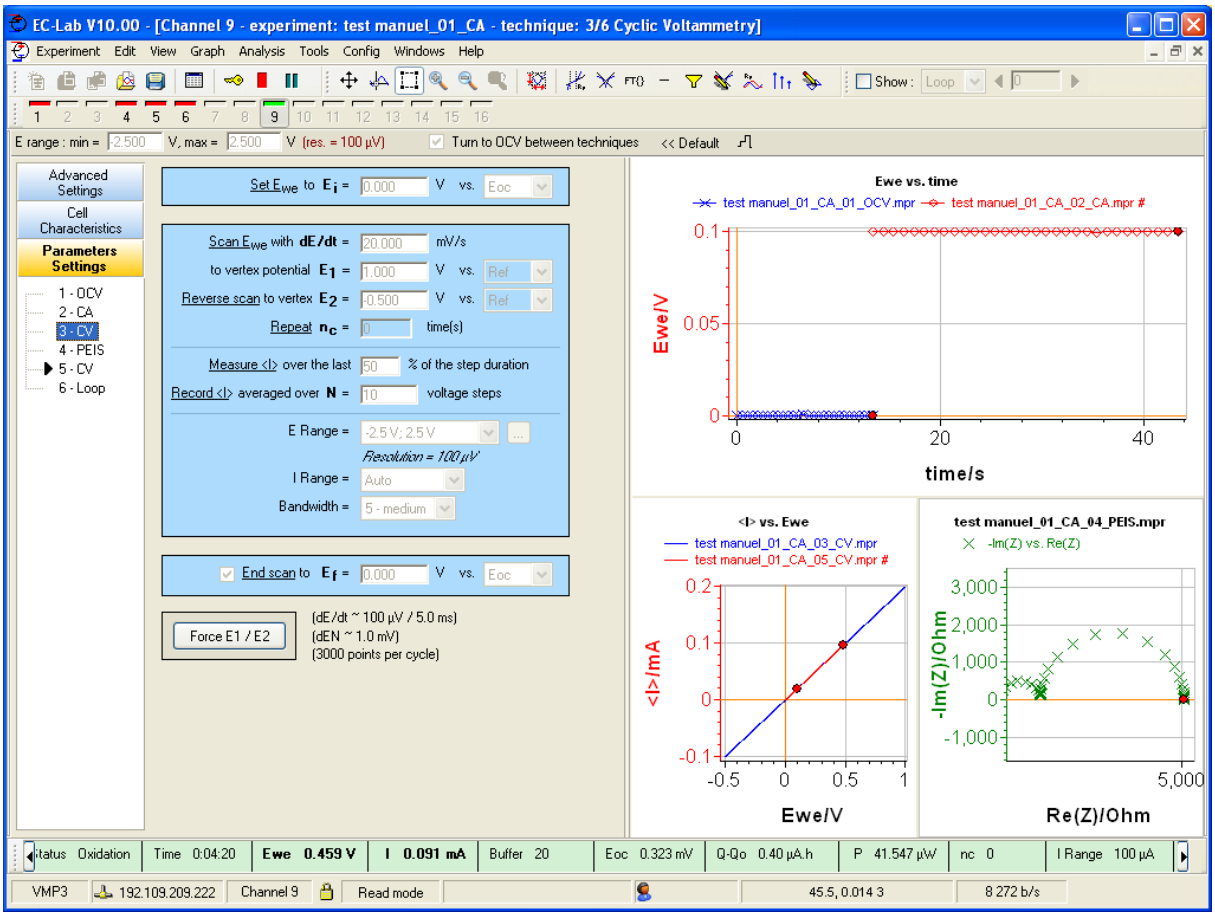


Fig. 203: Linked experiments window.

The linked techniques are displayed on the left of the window with their number in the experiment. Click on the button corresponding to the technique you want to see to display the detailed diagram.

Once the file name typed the acquisition starts, and the program shows the graphic display with the data files.
During the run the technique in progress can easily be identified by a green color around the corresponding button. Its number is displayed in the **running experiment** box (see next figure) as "**Run Tec**". The number of loops executed is displayed as "**Tec Loop**".
As for a single experiment run, it is possible to **Pause/Resume** and **Stop** the experiment. The **Stop** button will terminate the whole experiments acquisition. Nevertheless, one can stop the current experiment and continue to the next one with the **Next Exp** button in the tool bar.

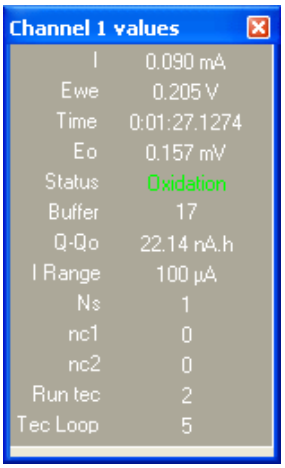


Fig. 204: Linked experiment current values.

Notes:

- The ZRA, MUIC protocols and the manual controls cannot be linked.
- The Polarization Resistance process calculation can be performed on the protocol linker loops separately.

Linked experiments settings can be saved with **Experiment, Save As,** or on the right click menu with **Save experiment…** and reloaded with **Experiment, Load settings...** or with the right click menu **Load settings...**.
Linked experiments settings files are text files with the *.mps extension like the standard settings files.

Be careful with the auxiliary signals recorded on Analog In1 or Analog In2 during linked experiments. Impedance techniques do not allow the recording of external signals. So if external signals are recorded during a linked experiment including impedance measurements, no external data points will be recorded during the EIS measurement period. When the user accepts such an experiment settings, the following warning message appears:

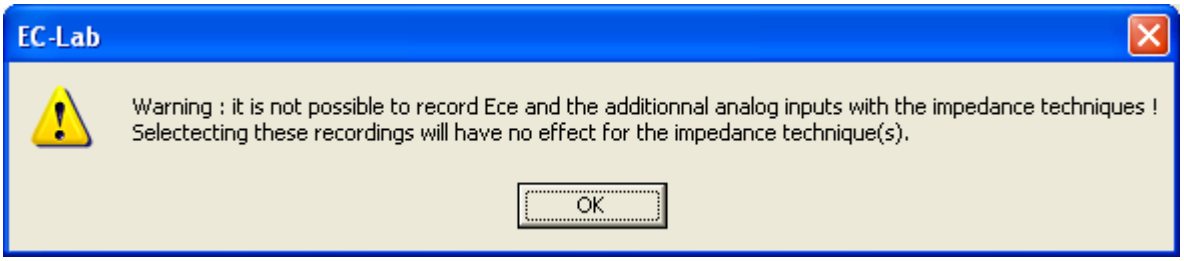

EC-Lab
Warning : it is not possible to record Ece and the additionnal analog inputs with the impedance techniques !
Selectecting these recordings will have no effect for the impedance technique(s).
OK

Fig. 205: Warning message on Analog signals recording with EIS techniques

4.2.2 Application of linked experiments with ohmic drop compensation

The following experiment is given as an example of linked experiments but also to show how to use the Ohmic drop compensation techniques. This experiment is composed of CA, CV, PEIS and Loop techniques.
This series of linked experiments is dedicated to illustrate the ohmic drop compensation. Indeed to compensate the ohmic drop during an experiment, the ZIR technique has to be set before the technique in which the compensation has to be done. To illustrate this the Fig. 206 is given as an example. In the left side of the figure, the series PEIS + CV + ZIR CV of

experiment is defined. On the right side of the figure, the second graph shows the superimposition of two CV graphs: one compensated and one uncompensated.

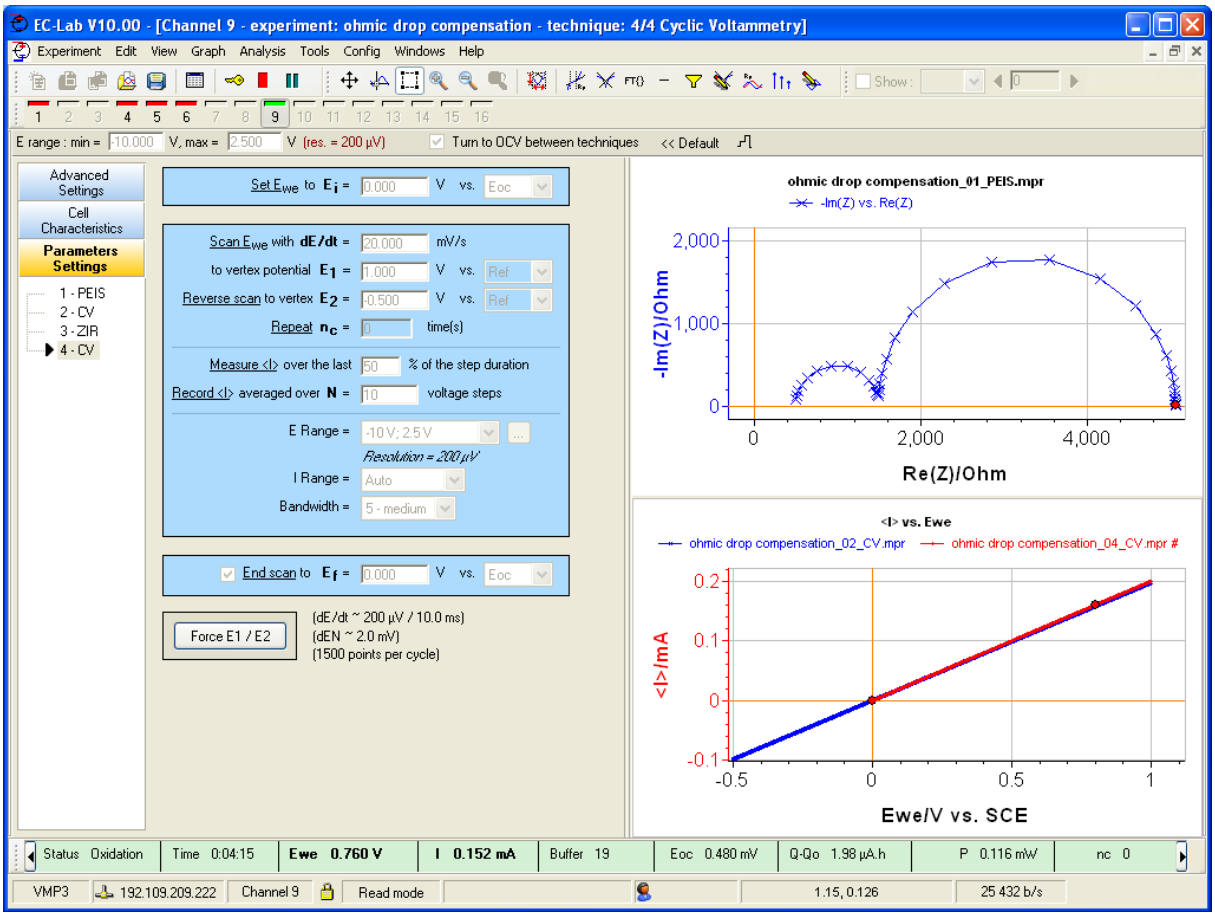

EC-Lab V10.00 - [Channel 9 - experiment: ohmic drop compensation - technique: 4/4 Cyclic Voltammetry]
Experiment Edit View Graph Analysis Tools Config Windows Help
Advanced Settings
Cell Characteristics
Parameters Settings
1 - PEIS
2 - CV
3 - ZIR
4 - CV
Set Ewe to Ei = 0.000 V vs. Eoc
Scan Ewe with dE/dt = 20.000 mV/s
to vertex potential E1 = 1.000 V vs. Ref
Reverse scan to vertex E2 = -0.500 V vs. Ref
Repeat nc = 0 time(s)
Measure <I> over the last 50 % of the step duration
Record <I> averaged over N = 10 voltage steps
E Range = -10 V; 2.5 V
Resolution = 200 µV
I Range = Auto
Bandwidth = 5 - medium
End scan to Ef = 0.000 V vs. Eoc
Force E1 / E2
(dE/dt ~ 200 µV / 10.0 ms)
(dEN ~ 2.0 mV)
(1500 points per cycle)
ohmic drop compensation_01_PEIS.mpr
-Im(Z) vs. Re(Z)
-Im(Z)/Ohm
Re(Z)/Ohm
<I> vs. Ewe
ohmic drop compensation_02_CV.mpr
ohmic drop compensation_04_CV.mpr #
<I>/mA
Ewe/V vs. SCE
Status Oxidation
Time 0:04:15
Ewe 0.760 V
I 0.152 mA
Buffer 19
Eoc 0.480 mV
Q-Qo 1.98 µA.h
P 0.116 mW
nc 0
VMP3
192.109.209.222
Channel 9
Read mode
1.15, 0.126
25 432 b/s

Fig. 206: Linked experiments example with ohmic drop compensation technique.

5. Advanced features

5.1 Maximum current range limitation (2.4 A) on the standard channel board

5.1.1 Different limitations

VMP2, BiStat, VMP3, VSP are designed to accept a maximum continuous current of 400 mA (*) on the 1 A current range for each channel and for a room temperature of 25°C. Note that the maximum current that can be reached in continuous by the SP-150 is 800 mA and 500 mA the SP-200 and SP-300.

In particular conditions of current and time, this limit can be passed. Then, the following message is displayed:

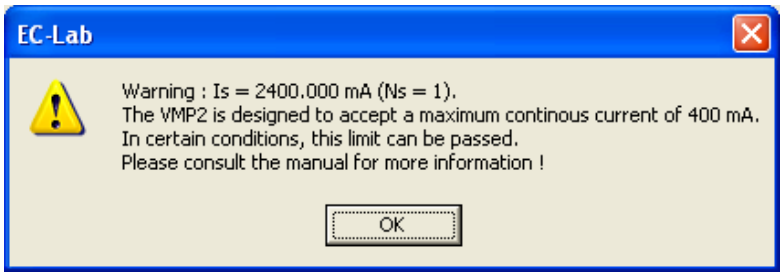

EC-Lab
Warning : Is = 2400.000 mA (Ns = 1).
The VMP2 is designed to accept a maximum continous current of 400 mA.
In certain conditions, this limit can be passed.
Please consult the manual for more information !
OK

Fig. 207: Warning message for the current limitation.

To go over 400 mA (*), one must respect three limits that depend on the maximum continuous current duration, the average current, and the power supply:

1) The maximum continuous current (I) is limited to 2.4 A for a maximum duration (t) of 2 ms and must respect $It \leq 4.8x10^{-3}\ A.s$ (**).
   For example, one can apply 2.4 A for only 2 ms and 1 A for 4.8 ms (see below). Beyond these limits a protection mode sets up in the instrument.

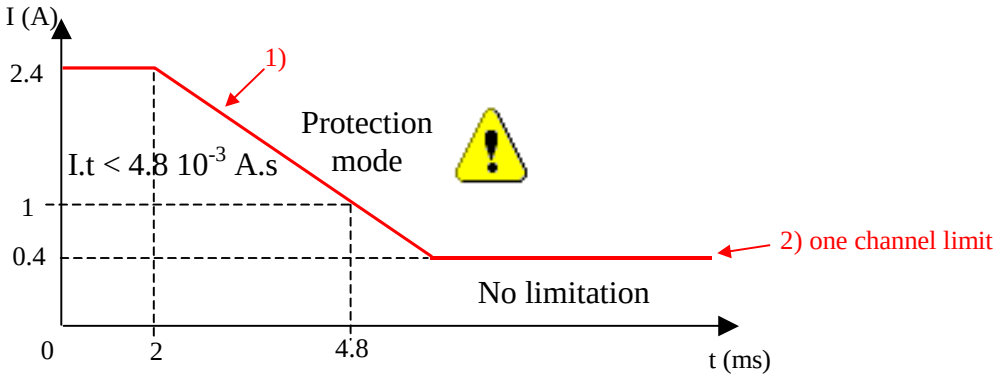


Fig. 208: Safe operating area.

2) The maximum average current <I> recommended during the experiment is 400 mA for one channel. For example in the protocol described on the following figure, two

different currents (I_1 and I_2) are applied for two durations (t_1 and t_2 respectively). The average current on a period is defined by:

$$\langle I \rangle = \frac{I_1 t_2 + I_2 t_2}{t_1 + t_2}$$

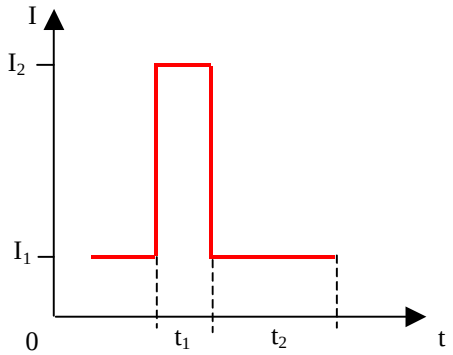


Fig. 209: Example of a current pulse protocol.

3) The power supply has a limit of 10 A. To avoid having the instrument enter the protection mode, the user must respect the following equation:

$$\sum_{1}^{Nb} I_{inst} \leq 10 \text{ A}$$

where Nb is the number of channels used simultaneously in the experiment and I_{inst} is the current measured for each of those channels.

For example, the number of channels used simultaneously in a 2.4 A current pulse protocol is limited to 4. It can increase to five if the maximum current is 2 A.

(*) for the instruments sold after **April** 2004. For the others, the limit is 250 mA.
(**) for the instruments sold after **April** 2004. For the others, the limit is 2.4 10^{-3} A.s.

Note that the same principle is applied on all the I Range values (except the 1 A range) of SP-200 and SP-300.

5.1.2 Application to the GSM battery testing

A specific current pulse profile is used for GSM battery testing. The GSM pulse protocol (see next figure) consists of applying a current pulse (I_1 between 1 and 2 A) for a short time ($t_1 \leq 1$ ms) followed by a step to a lower current (I_2) for a longer period (t_2).

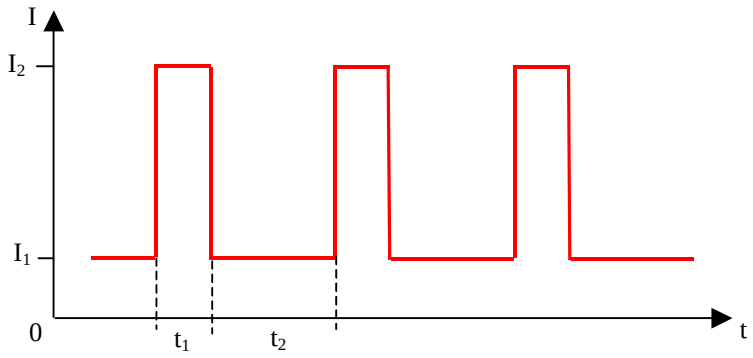


Fig. 210: Theoretical GSM pulse waveform.

This theoretical pulse waveform can be easily programmed into EC-Lab® with the chronopotentiometric protocol. The sequences are presented in the table below:

- Ns = 0: OCV
- Ns = 1: apply 1.4 A for 1 ms
- Ns = 2: apply 0.3 A for 10 ms

The sequence is repeated few times. The period is 11 ms and <I> never exceed 400 mA.

Ns	Is	unit Is	dIs	unit dIs	ts (h:m:s)	EM (V)	dQM (mA.h)	dEs (mV)	dts (s)	I Range
0	0.000	mA	0.000	mA	0:00:0.0000	pass	0.000000	0.00	0.0000	1 A
1	1.400	A	0.000	mA	0:00:0.0010	pass	0.000389	0.00	0.0002	1 A
2	0.300	A	0.000	mA	0:00:0.0100	pass	0.000833	0.00	0.0002	1 A
3										

Fig. 211: Table of the experiments for GSM battery testing.

The result is represented on the following figure.

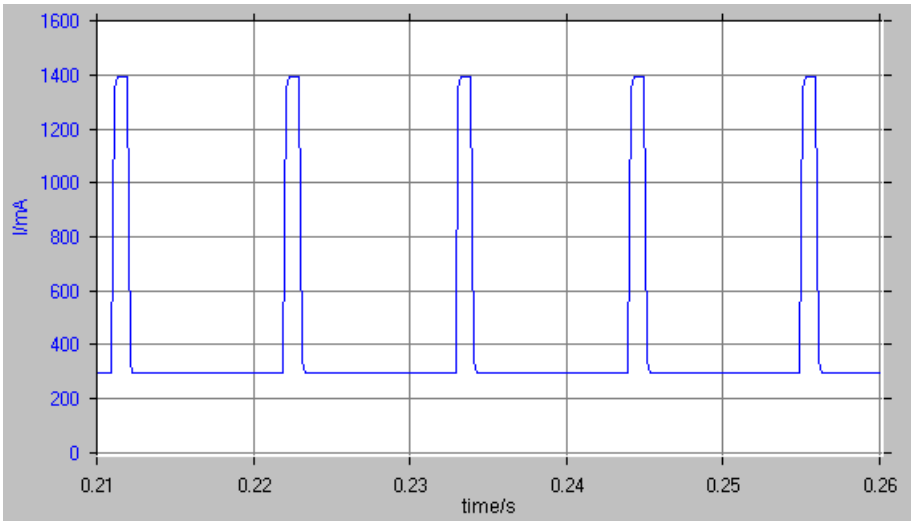


Fig. 212: GSM pulse waveform generated by chronopotentiometric protocol.

5.2 Optimization of the potential control resolution

5.2.1 Potential Control range (span)

Our potentiostats/galvanostats are digital instruments. The potential is applied to the cell via a 16 bit DAC (Digital to Analog Converter). The DAC delivers a potential in the ± 10 V range for VMP3, VSP, SP-150 and in the ± 10.9 V range for SP-200 and SP-300 with a resolution equal to its LSB (Least Significant Bit) that corresponds to the smallest potential step available, and is defined as:

$$LSB = \frac{20\,V}{2^{16}-1} = \frac{20\,V}{65535} = 305.18\ \mu V \text{ for VMP3 family,}$$

and as $LSB = \frac{21.8\,V}{2^{16}-1} = \frac{21.8\,V}{65535} = 333.33\ \mu V$ for SP-200 and SP-300.

When the user enters in EC-Lab® a potential value E_{ctrl}, the value sent to the DAC is a 16-bits value corresponding to an integer number of LSB, i.e. defined as:

$$E_{cell} = N.LSB with\ N = round\left(\frac{E_{ctrl}}{LSB}\right)$$

where “round” is the function that returns the nearest integer of the variable.

Usually, experiments do not require 20 V potential ranges.

So in EC-Lab®, the potential control resolution can be adjusted to the required experimental potential range, in order to have potential values as close as possible to the set values, and in potential sweeps, to be as close as possible to a linear sweep with the smallest potential step.

This is obtained by adjusting of the DAC output from ± 10 V (± 10.9 V) to the required potential range, through a programmable attenuator and a programmable offset.

This optimization is available at the top of the "**Parameters Settings**" window (see below).
Given the E_{max} and E_{min} limits, the potential range is reduced to E_{max} – E_{min} and the potential resolution becomes:

$$\frac{E_{\max} - E_{\min} + 0.2}{65535}$$

Adding the 0.2 V value is a hardware constraint to allow reaching E_{max} and E_{min}.
Thus the theoretical maximum resolution is ~ 3 µV (200 mV / 65535).
In EC-Lab®, we have chosen to have a set of fixed resolution values adjusted to the potential range in a 1-2-5-10 scale.
This leads to the table below, for the maximum potential range values at which the resolution changes.

$E_{max} - E_{min}$ (V)	Resolution (µV)
20	305.18 or 333.33
19.46	300
12.9	200
6.3	100
3.0	50
1.1	20
0.4	10
0.12	5

Table 1: Resolution values according to the E_{we} potential range.

Note that the potential control resolution is available with low current boards delivered from 1st June 2004. For the other low current boards (delivered before 1st June 2004), a technical modification is necessary.

5.2.2 Setting of the Working Potential window

If no experiment limits are defined the potential resolution is 305.18 µV (or 333.33 µV), corresponding to the ± 10 V (± 10.9 V) range. E Range is located in the setting of each technique since EC-Lab® version 10.00.

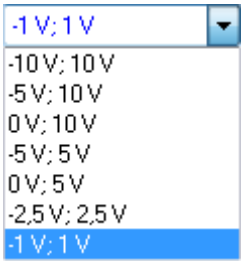


Fig. 213: E Range selection.

Using the “Edit” button opens a window to define the potential range manually. Entering the required E_{we} min and E_{we} max the corresponding value of the potential control resolution appears. For example entering 0 V and 1 V leads to 20 µV resolution.

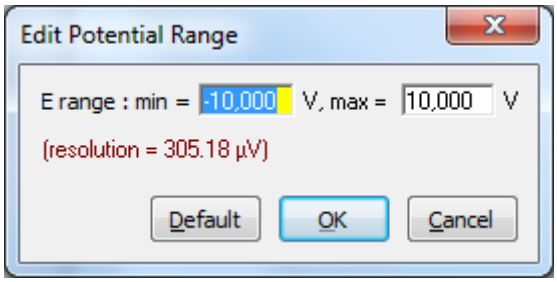


Fig. 214: Edit potential range window.

Application

Optimization of the potential resolution is particularly interesting when trying to perform protocols based on potential scan, such as CV, in order to approach linear scans as much as possible.

For example, after choosing the above 1 V potential window and loading a CV a 20 µV potential step value is automatically proposed when entering a scan speed dE/dt, as shown in Fig. 215 below.

Fig. 215: CV experiment, potential scan with 20 µV steps.

5.3 Measurement versus control current range

Our potentiostats are designed to work either in the potentio (static or dynamic) mode or in the galvano (static or dynamic) mode. In the potentio mode, the potential between the working and the reference electrode is controlled. The current resulting from the redox processes at the applied potential is measured. On the contrary, in the galvano mode the current is controlled, and the potential is measured. In both cases, one variable is controlled and the other one is measured. The current and the potential dimensions always have to be adjusted while choosing the range in which the experiment is performed. In fact, the result accuracy will be better if the range is chosen closer to the experiment's limits.

5.3.1 The potentio mode

The potential control range can be adjusted for the experiment with the experiment limits E_{max} and E_{min} (see the installation and configuration manual for more details). The result of this adjustment is the potential resolution increase (from 300 µV to 5 µV). In this control mode, the user must define the measurement current range. The closer to the experiment the current range is, the better the measurement accuracy. The maximum current value that can be measured corresponds to 2.4 times the chosen current range. In other words, for the 10 µA range on the figure below, the user can apply potentials from – 10 to + 10 V and he can measure currents going from – 24 to + 24 µA with no restrictions. .

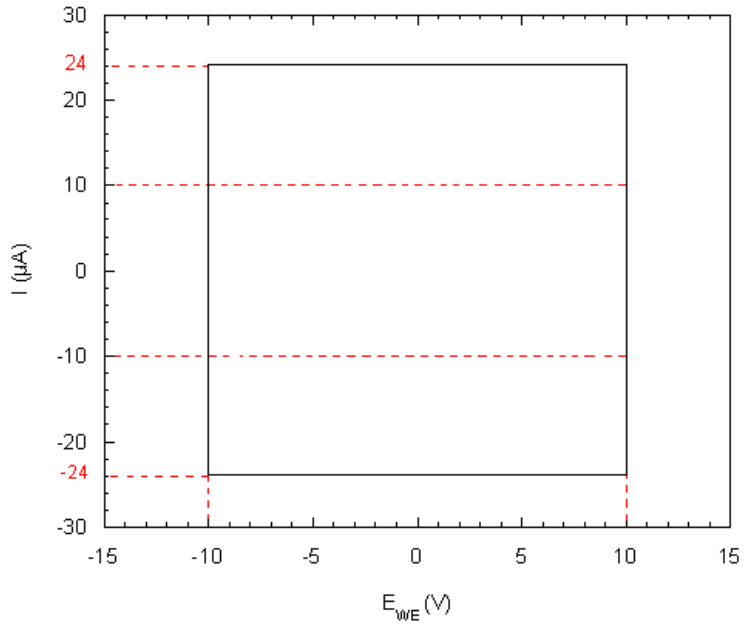


Fig. 216: Current versus Potential available domain in the potentio mode.

5.3.2 The galvano mode

In this mode the current range must be adjusted to the controlled current. In that case, the user must distinguish the 1 A current range (which will be discussed in the following part)

from the others (please refer to the part 5.1 page 163 for more details). Usually the controlled current value cannot bypass the range. If the user wants to apply 15 µA current to the cell, he must choose the 100 µA current range.
But with all the instrument of the Bio-Logic range, the user can bypass the current range in the control mode in a limit of 2.4 times the range with several conditions on the potential. In the galvano mode, when the controlled current value is higher than the range, the measured potential range is reduced to ± 8.6 V instead of ± 10 V whatever is the chosen current range (see figure below).

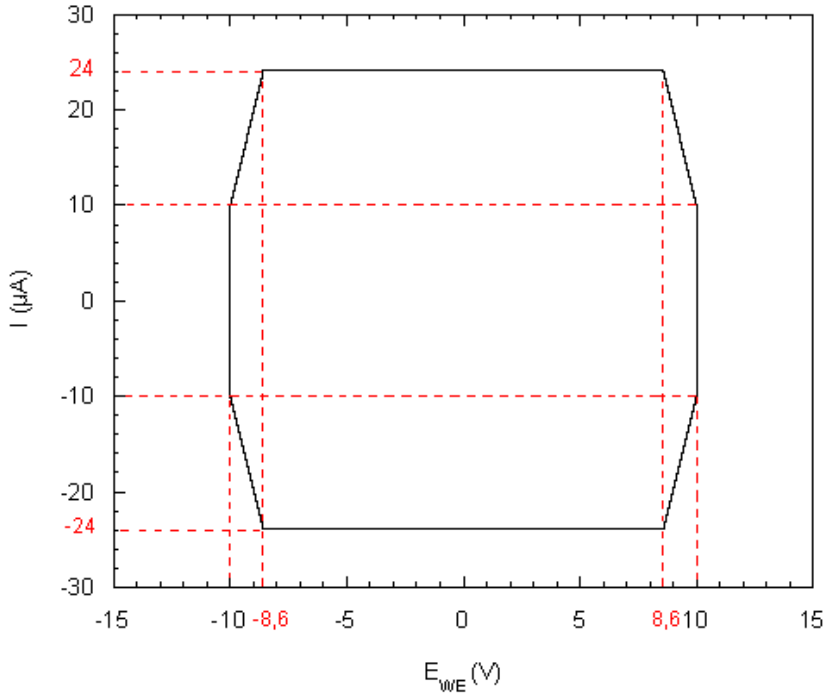


Fig. 217: Current versus Potential available domain in the galvano mode.

5.3.3 Particularity of the 1 A current range in the galvano mode

The 1 A current range is a very special range. The label (1 A) of this range has been chosen according to the control in the galvano mode and the measurement in the potentio mode. In the galvano or potentio mode, the channel board structure limits the maximum continuous applied or measured current to 400 mA (800 mA for SP-150 and 500 mA for SP-300). But in certain cases the user can bypass this value to apply or measure current pulses up to 2.4 A (corresponding to 2.4 times the 1 A range). The average current for either measurement or control must not bypass 400 mA (800 mA for SP-150 and 500 mA for SP-300). This is especially used for GSM battery testing (Please refer to the part 5.1 page 163 for more details)

Warning: the low current board cannot accept more than 400 mA in potentio and in galvano mode. We advise the users to be mindful of the maximum current when using low current boards.

5.3.4 Multiple current range selection in an experiment

The EC-Lab® software offers a facility to select different current ranges in either galvano or potentio mode for an experiment. The experiment can be made with only one technique but with several sequences in the technique or with linked techniques. In both cases, the user can choose different current ranges between sequences or between techniques if an OCV period is set between them.

For example, in a GCPL experiment with 10 sequences, the user can select 10 different current ranges if the third block of OCV is activated into every sequence. Then a warning message is displayed:

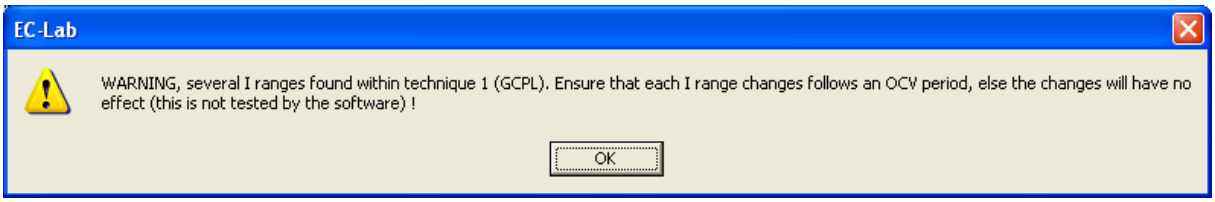

EC-Lab
WARNING, several I ranges found within technique 1 (GCPL). Ensure that each I range changes follows an OCV period, else the changes will have no effect (this is not tested by the software) !
OK

Fig. 218: Warning message on different current ranges into a setting.

Note: when several current ranges are selected in a setting the software will not test if some OCV periods are set between sequences. It is the user's responsability.

5.4 External device control and recording

5.4.1 General description

EC-Lab® software enables the user to control external devices such as rotating electrodes and thermostatic baths and record external analog signals through the auxiliary DB9 connector. The user must configure the output to control an external device and configure Analog In1 and Analog In2 inputs to record external signals. Our instruments can control and record analog signals from – 10 to + 10 V. Most of the external devices work in a 0 to + 5 V range. The figure below shows the external device window where the user sets parameters. Many instruments are already configured in the software to be controlled by our potentiostats. The list will be completed in the future versions of EC-Lab® software. To configure external devices, select "**External Device**" in the "**Config**" menu. The following window is displayed:

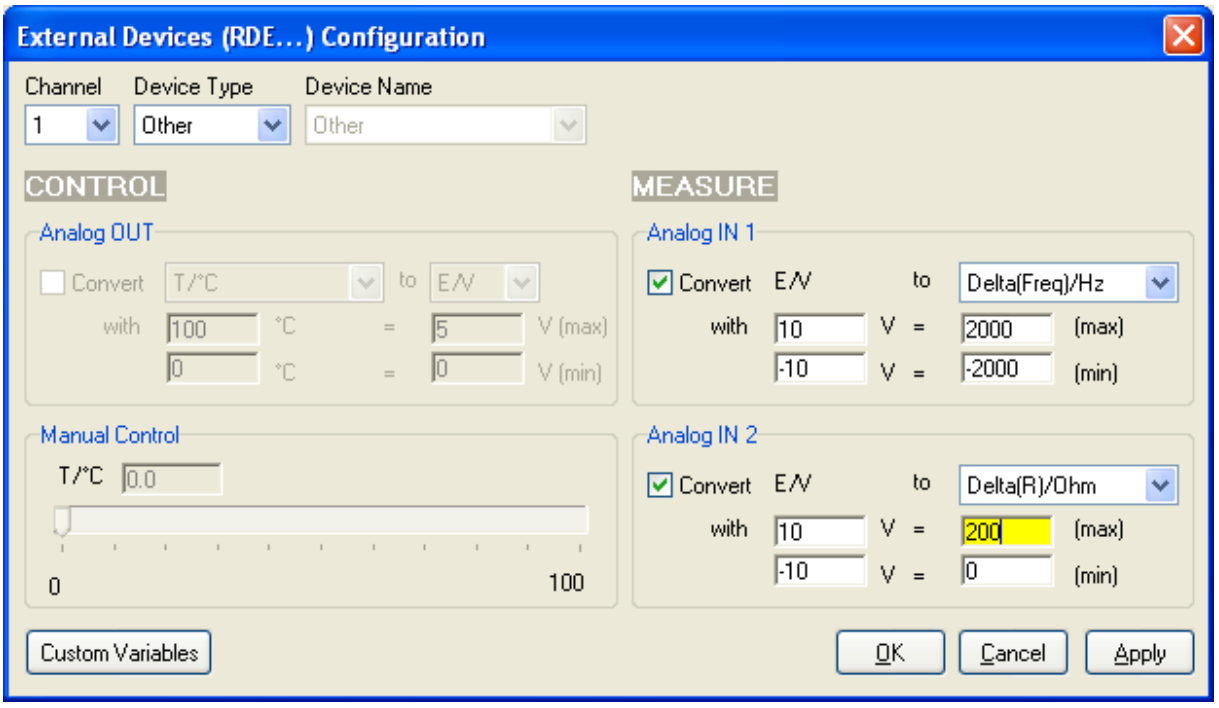


Fig. 219: External device configuration window.

The user must define several parameters to configure the external device to either be controlled via the analog output (left column) or record/measure data via analog input 1 and 2 (right column). The procedure for the configuration of the auxiliary inputs/outputs is described below:

1- Choose the channel to configure. Each channel can be configured for a specific device. One channel can control one device and the other one another device.
2- Select the Device Type in the list between None, Thermostat, RDE, QCM and other. One or several device names are available according to the selected device type.
3- Among the available devices, some can be controlled with the analog output and some of them can only be used to record values with analog inputs 1 and 2. The user must tick the box to activate the input/output.
4- In the activated frame, the user must define the conversion between the input voltage and the variable to plot. This is a direct linear conversion in the range defined by the user between the min and the max value.
5- The user can also define the name and the unit of the variable he wants to display. Click on "**Custom Variables**". The figure below is displayed:

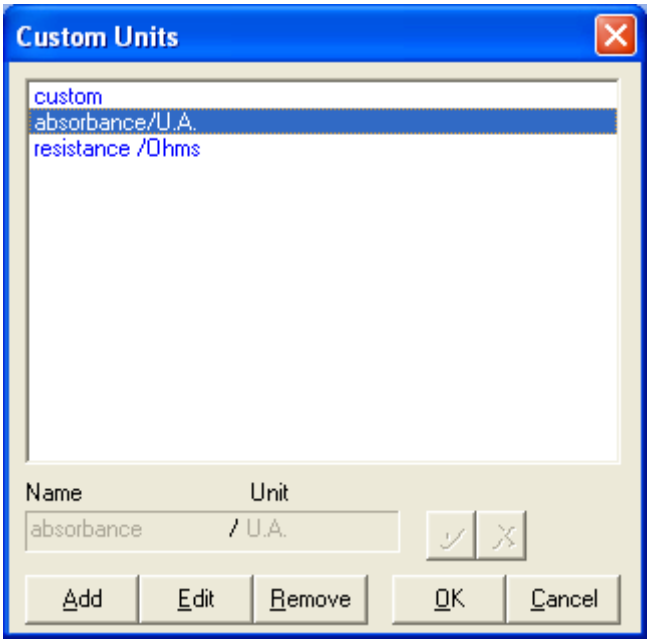


Fig. 220: Custom Units window to define new variables.

To create a new variable with its unit, click on "**Add**" and put the name and the unit of the new variable in the frame. Then click on to validate. The new variable appears in the list in blue (as a custom variable) and can now be selected as the recorded variable for the analog inputs.

6- Finally, click on "**Configure**" to configure the selected channel to record the auxiliary input signal

The new selected variables for Analog In1 and Analog In2 are automatically displayed in the "Cell characteristics" window and activated for recording. In the "**Selector**" the created variables are displayed and can be plotted. These auxiliary variables can be used in several protocols as conditional limits of an experiment.

Note: - The parameters set in Analog In1 and Analog In2 to define the linear slope can be inverted to have an opposite variation of the recorded value with the plotted value.
- The configuration of external devices that can be controlled by the potentiostat (analog output) are described in detail in the corresponding sections of the manual.
- A manual control of external devices is also available on the right of the panel.
- When a channel has been configured to control an external device, this device can be seen in the global view.

5.4.2 Rotating electrodes control

The standard instrument equipped with channels delivered since November 2004, with or without boosters can control a rotating electrode such as a ALS-RRDE-3A RRDE Rotating Disk electrode model with the auxiliary input/output. A specific control panel has been designed to control the rotating speed. Note that no measurement of the rotating speed is available. This model of rotating electrode is designed to work either one or two working electrodes (ring-disk electrodes). A bipotentiostat is necessary for the measurement of the working electrode potential of both electrodes. The VMP3 (using two channels), VSP, SP-300 or the BiStat are appropriate instruments for this kind of experiment.

Fig. 221: RRDE Rotating Disk electrode ALS RRDE-3A.

5.4.2.1 Control panel

Before running any experiment with a rotating electrode, one must first choose the rotating unit. Select **Config \ External Device (RDE…)…** in the EC-Lab® main menu:

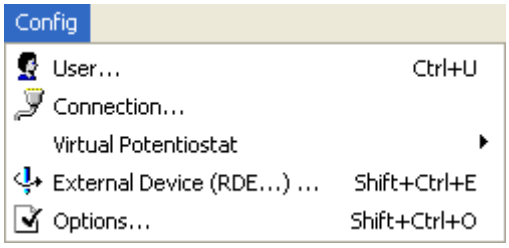


Fig. 222: Menu to choose for rotating electrode control.

Note: this menu is available only if channels designed to drive a RDE (since 11/04) are connected with the RDE electrode rotator. Then the following window is displayed:

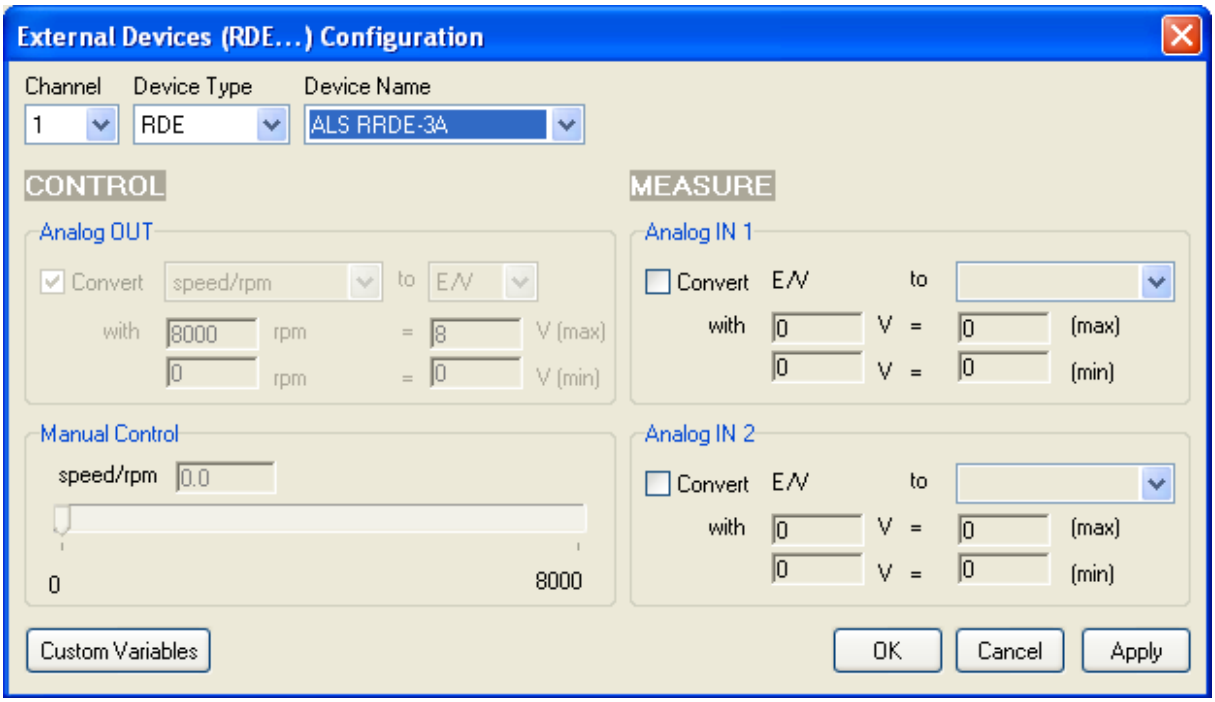
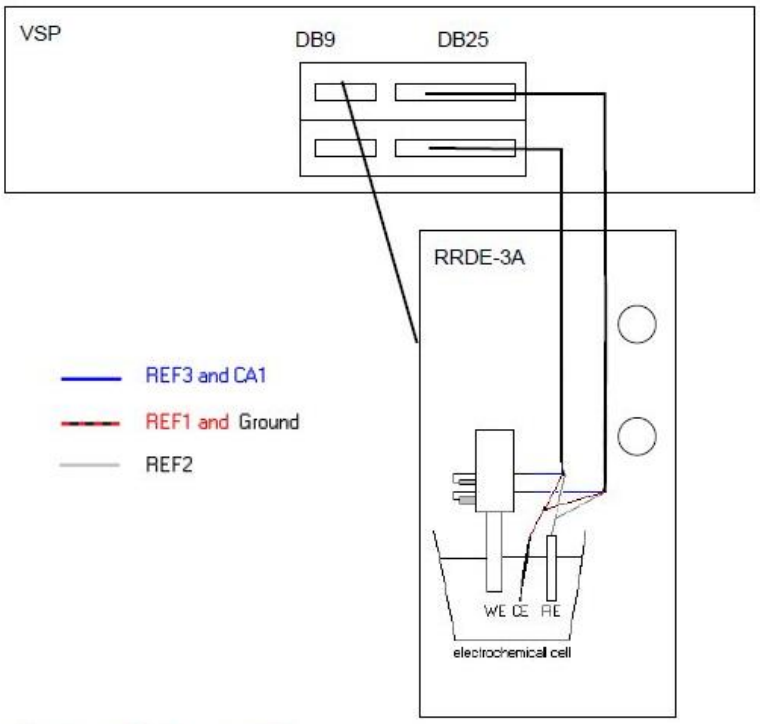


Fig. 223: Rotating electrode control configuration

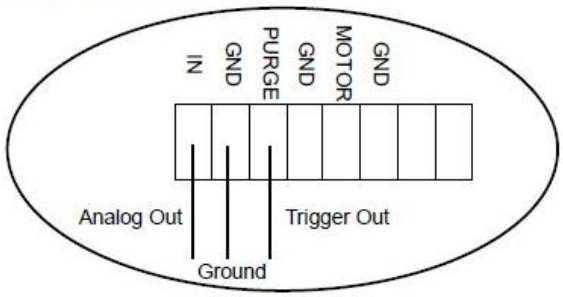
Under **Speed control unit**, one can select the standard supplied ALS RRDE-3A or PINE RRDE or RADIOMETER CTV101 electrodes rotator. For these devices, the calibration parameters are factory set. Other external systems can be used but are not available. They will be added to the list upon request. Note that calibration parameters for an already selected device are not available. Nevertheless if you select another device, it is possible in the "**Analog OUT**" window to define the control parameters. Click on the **Apply** button to validate the settings. Note that this menu can be activated without any rotating electrode unit, but will only have effects for the electrochemical instruments equipped with a rotating system.

In order to use two potentiostat/galvanostat channels and some rotating ring-disk electrode (with two working electrodes), it would be useful for the user to synchronize both channels

together in order to start the experiment on both channels at the same time. Report to the corresponding part in the manual for more information about the synchronize option.



Focus on the rear panel:



5.4.3 Temperature control

Temperature control is possible with the auxiliary inputs/outputs of a VMP3 with a voltage control. Several thermostats have already been configured on the VMP3 such as Julabo series and Haake Phoenix series.

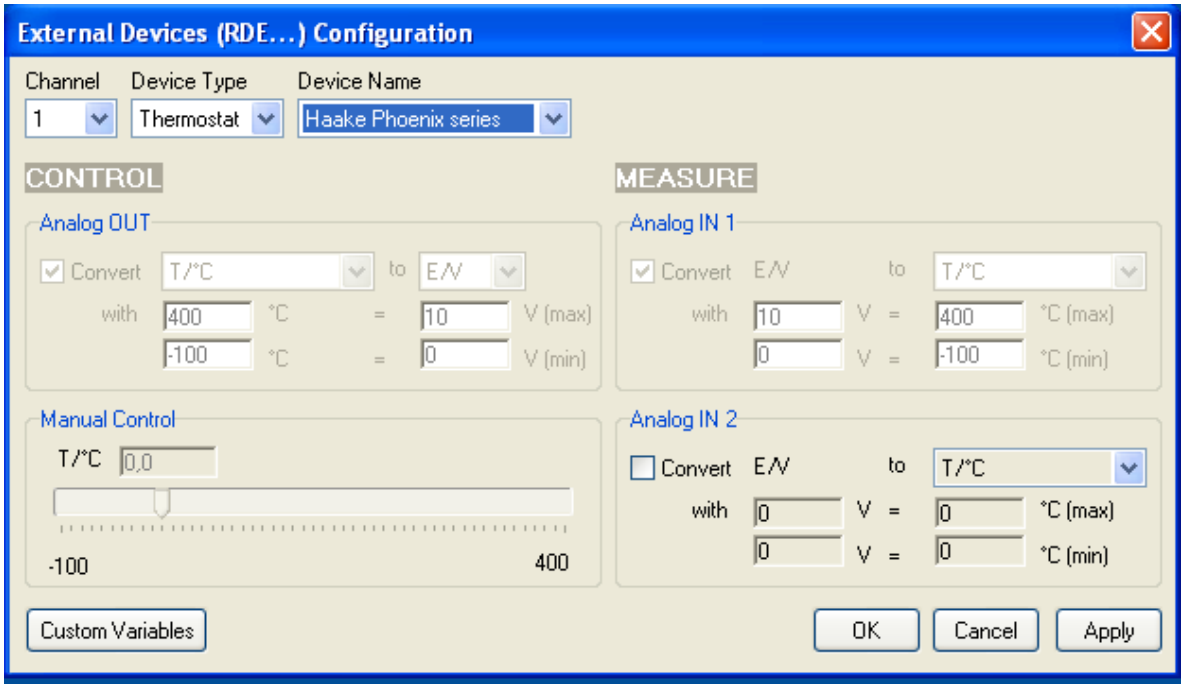


Fig. 224: Haake Phoenix series thermostat control configuration with a VMP3.

The user can configure other thermostats to only record temperatures (Analog in) or both control (Analog Out) and record (Analog In) temperature.

5.4.4 Electrochemical Quartz Crystal Microbalance coupling

The SEIKO EG&G QCM 922 quartz crystal microbalance has been coupled with our potentiostat/galvanostat to record both the frequency variation and the resistance variation. The configuration for the EQCM coupling is described in the figure below:

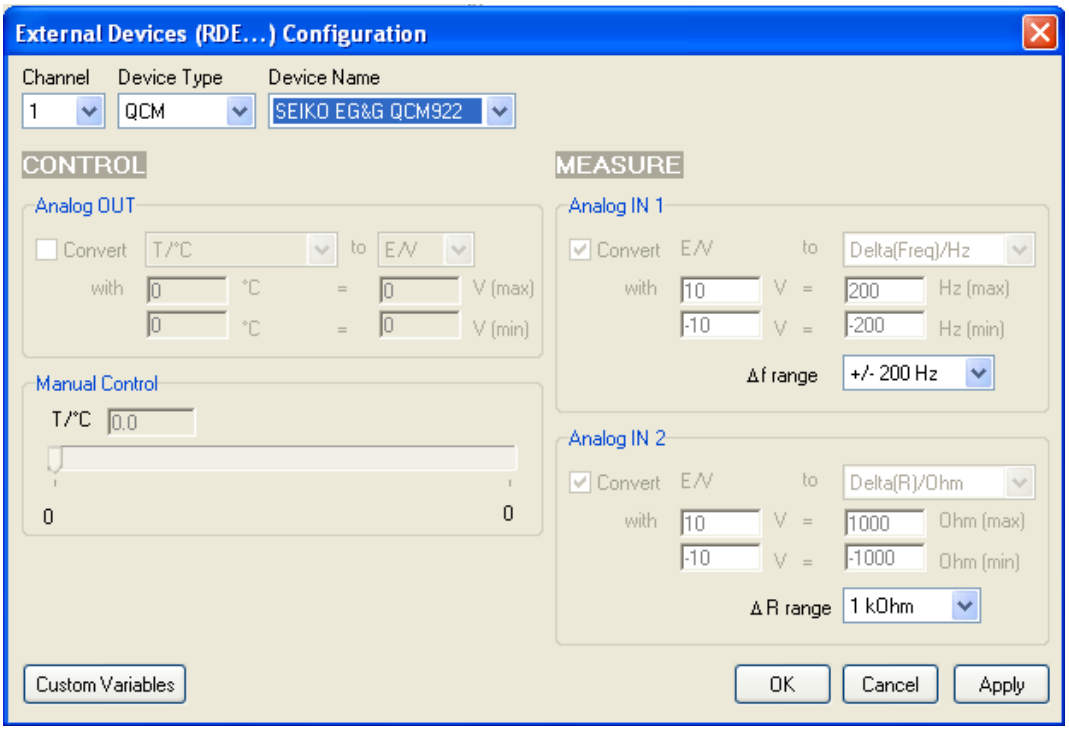


Fig. 225: SEIKO EG&G QCM 922 configuration window.

One can see that both frequency and resistance variations are recorded on the potentiostat analog inputs. The user must define both the frequency range and the resistance range. The results of this experiment are displayed below (Fig. 173):

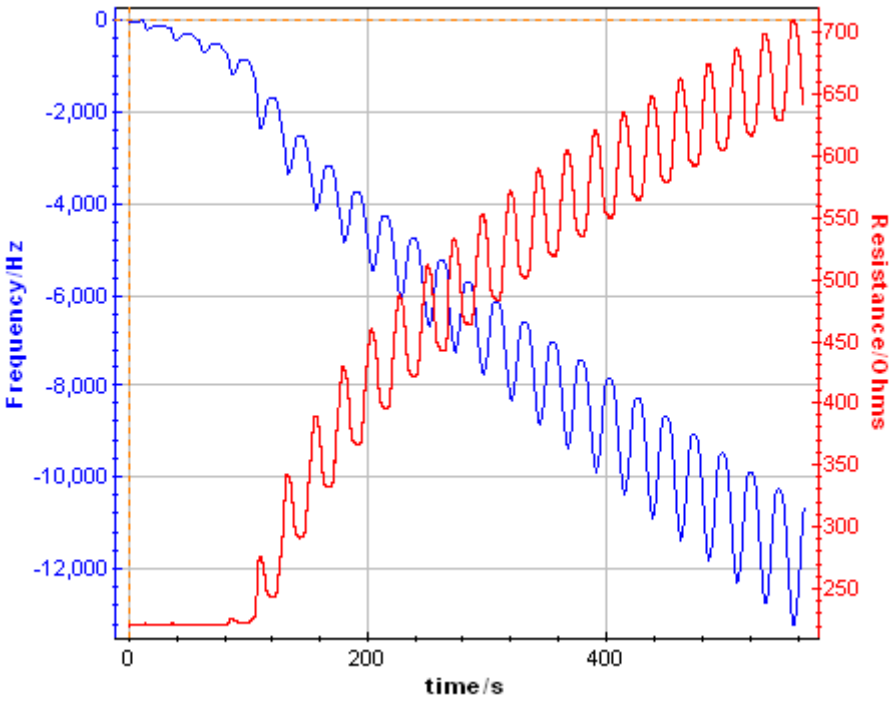


Fig. 226: Frequency and resistance variations recorded from the analog inputs for a VMP3 coupled with a SEIKO EG&G QCM 922.

A process is also available to calculate the amount of a species electro-disposed on the quartz. To use this process, select the process data option in the Analysis menu.

5.5 Preconditioning methods before an electrochemical experiment

An electrochemical experiment generally contains several stages that can be combined in the following order: 1) experiment installation, 2) equilibrium state establishment or preconditioning, and 3) electrochemical measurement. The first and third stage can follow each other without the second one. However, the user often needs to do preconditioning stages before the electrochemical measurement. The nature of these stages is related to the electrochemical system to study and the electrochemical technique used (mainly analytical or plating electrochemistry). We will consider in this chapter the equilibration and preconditioning steps in the electrochemical cell (electrode polishing, sonication steps or other surface treatments are not considered).

5.5.1 Equilibrium state establishment

The equilibrium state establishment is considered a stage where no constraint is applied to the system (neither in the electrochemical cell solution nor on the electrode surface).
The usual protocol for this consists of applying an Open Circuit Voltage period. This period can be seen as a waiting duration until the electrode or the cell has come to equilibrium with the ability for potential recording (for example, to follow the equilibration of a battery). The user can set a limit to the OCV period with a minimum potential variation in time (that can be compared to the equilibrium).

5.5.2 Preconditioning methods

The preconditioning steps can be divided into two different categories. The first one is to carry out a mechanical modification without applying any electrochemical signal. The second one is to apply an electrochemical signal in order to modify the working electrode surface.

5.5.2.1 Mechanical modification

Mechanical modifications gather all the preconditioning steps of the electrochemical solution without applying any electrical constraint to the system (OCV period). This includes:

- A deaeration period (with nitrogen or argon) of the electrochemical cell with a mechanical stirring.
- A necessary period for a stationary state establishment (with stirring).
- In the case of fuel cells, the membrane incubation with a gaseous flux on the electrodes without generating an electrochemical reaction.

5.5.2.2 Electrochemical modifications

These modifications require an electrochemical constraint (by applying a potential or a current) at the electrode surface. The applied potential is commonly the starting potential of the electrochemical measurement. Different reasons for applying the starting potential can be mentioned:

- preconcentration (accumulation) of electroactive species on the electrode surface (for example for metals while reducing on the electrode surface before an anodic stripping voltammetry detection).
- Treatment of the electrode surface (activation of electroactive functions or cleaning) at a fixed potential or current value or in a dynamic mode with varying E or I.
- To avoid a great transient current (or potential) when the experiment will start. In that case, the working electrode will move from the equilibration potential to the starting potential (that can be very different).

5.5.3 EC-Lab® facilities for the pretreatment before an electrochemical measurement

To perform preconditioning with EC-Lab®, the user must use one of the following protocols: OCV, Chronoamperometry, Chronopotentiometry, Modular Potentio MP or Modular Galvano MG (for a detailed description see the corresponding section in the techniques and applications manual).
Particularly, modular potentio and modular galvano are very useful protocols for preconditioning before the experiment. Thus the modular potentio mode allows the user to apply a defined potential for a given time (potentiostatic mode) and record other variables. The modular galvano mode allows the user to apply a particular current for a given time (galvanostatic mode) and record other variables. The potentio or galvano dynamic modes allow the user to apply a potential or a current ramp respectively.

6. Troubleshooting

6.1 Data saving:

Problem: Data cannot be saved from a given channel (this channel appears in yellow into EC-Lab®, and the program displays an error message while attempting to save data):
Solution(s):
- ensure that the saved file has not be moved, destroyed, opened by another application.
- if the saved file is on a network drive, ensure that you have the right to write data into the same directory (create and destroy a text file). Else see your network authorizations…
- in EC-Lab®, select **File, Repair...** Then select the saved file and click on the **Repair** button.
- ensure that the computer IP Address has not been modified since the beginning of the experiment.
- if the problem persists, contact us.

6.2 PC Disconnection:

Problem: The PC is disconnected from the instrument ("Disconnected" is displayed in red on the EC-Lab® status bar):
Solution(s):
- check the PC – instrument connection:
  - direct connection: verify that the crossed Ethernet cable is plugged from both ends.
  - network connection: verify that the yellow led is blinking on the instrument front panel and that you can access to your network directories from the PC.
- check that the green LED is blinking (this assumes that the multichannel potentiostat is always running properly).
- in the Tera Term Pro window type "r" or "R" : this will restart the Ethernet connection program that is a part of the instrument firmware.
  WARNING: this operation is not a simple task, so proceed like this only in case of trouble.
- if the problem persists, contact us.

6.3 Effect of computer save options on data recording:

Electrochemical experiments can often have a long duration (more than 24 hours). During the experiment, the computer should always be able to record the data points. If the user enabled the power save option for his hard disk, he risks being unable to record the points. In order to avoid this, we advise the user to remove the power save option from his computer in the settings panel.

7. Glossary

This glossary is made to help the user understand most of the terms of the EC-Lab® software and the terms mentioned in the manual. The terms are defined in the alphabetical order.

Absolute value: mathematical function that changes the negative values in positive ones.

Accept: button in EC-Lab® software that switches to "Modify" when the user clicks on. "Modify" must be displayed to run the experiment.

Booster: current power booster that can be added to each channel individually.

Apparent resistance (R_i): conventional term defining the electrolytic resistance in a solid electrochemical system such as a battery. R_i is defined as the ratio dE/dI when the potentiostat switches from an open circuit voltage mode to galvanostatic mode and vice versa.

ASCII file exportation: exportation of the raw data files or the processed data files to ASCII text format in order to use them with other software (new format: .mpt).

Axis: graphic function used to define the axis range, the logarithmic spacing and the grid lines.

Bandwidth: represents the frequency of the regulation loop of the potentiostat. It depends on the electrochemical cell impedance. The bandwidth's values go from 1 to 7 with increasing frequency.

Calibration: operation that must be done for each channel in order to reduce the difference between a controlled value (for example E_{ctrl}) and the corresponding measured value (for example E_{we}).

Capacity per cycle: processing function that calculates the capacity per cycle for the galvanostatic with potential limitation, the chronocoulometry / chronoamperometry, the cyclic voltammetry, and the potentiodynamic cycling with galvanostatic acceleration protocols.

CASP Fit: tool available with the graphic display used to fit a curve obtained with the Constant Amplitude Sinusoidal microPolarization technique. This tool is used to determine the current corrosion and the coefficients of corrosion.

Channels: each one of the boards corresponding to an independent potentiostat/galvanostat.

Characteristic mass: total mass of the species in the electrochemical cell in most of the cases. It is different from the mass of electroactive material. This mass is used in the graphic display to represent mass current density, or mass charge density.

Circle Fit: tool available with the graphic display used to fit a circular curve.

Compact: mathematical function allowing the user to compress data points from the raw data file. Compact functions are available with the GCPL and PCGA protocols. All points of each potential step are replaced by their average taken at the end of the potential step. The number of points of the compacted data file decreases a lot compared to the raw file.

Compliance: correspond to the potential range of the counter electrode versus the working electrode potential. This option is used in molten salt electrochemistry where the potential decreases a lot between the counter and the reference electrode.

CE to ground connection: also called N'Stat connection, this mode allows the user to lead measurements on eight working electrodes with one or eight reference electrodes and one counter electrode connected to the ground. It is a very useful tool for biosensors study. This mode can be activated in the "Advanced settings" window.

Corr. Sim.: this tool simulates corrosion curves obtained with the Linear polarization, Constant Amplitude Sinusoidal microPolarization or Variable Amplitude Sinusoidal microPolarization techniques.

Cycle: inside a protocol, this term is used to describe a sequence repeated with time.

Cycle number: processing function that allows the user to display on the graphic one or several cycles chosen in the raw file. The selected cycles are lightened and the others are hidden.

Cyclic voltammetry (CV): this protocol consists of scanning the potential of the working electrode linearly and measuring the current resulting from oxydoreduction reactions. Cyclic voltammetry provides information on redox processes, electron transfer reactions, and adsorption processes.

Default settings: settings defined and saved as default by the user and automatically opened when the corresponding protocol is selected.

Description: tab in the experiment selection window, which describes the chosen protocol.

Device: EC-Lab® software window in the "Config" menu used to add new instrument IP address to be connected to the computer.

EC-Lab®: software drives the multichannel potentiostats/galvanostat.

Electrochemical Noise Analysis: this tool is dedicated to analysis corrosion data and to determine the electrochemical noise presents on the data.

Electrode characteristics: in the "cell characteristics" window in EC-Lab®, the user can set all parameters about the electrode.

Electrode surface area: geometric surface of the working electrode. It is a value that is used to represent current density or charge density.

Experiment limits: in the "advanced settings" window, these limits can be used in two different ways and concern potential, current and charge. The first one is to protect the cell against damages. These limits must be higher than the limits set in the experiment. The second way to use these limits is the control potential resolution. It corresponds to smallest potential step that can be made according to the full potential range.

File-Export as text: function that converts the raw data file (.mpr) to a text format file (.mpt). The new created file is located in the same directory as the raw file.

File-Import as text: function that converts an ASCII file (.txt) created by other software into an EC-Lab® raw data file (.mpr). The new created file is located in the same directory as the text file.

File- Load: the "load" function allows the user to load a data file (.mpr), a settings file (.mps), a linked experiment settings file (.mpls) or a report file.

Filter: this filter can be used as off-line filter many times after the experiment but also just after the recording of the data by ticking a box on the Advanced Setting window. Many methods and windows are available.

Fit: graphic tool used to determine kinetic or experimental parameters.

Fourier Transform: tool used to apply a Fourier transform to recorded data, many windows are available.

Global view: EC-Lab® software window where all the channels are shown with the user, the experiment, the state (relax, oxidation, reduction), and the booster or low current board.

Group: option used in a multichannel mode to start different experiments on the selected channels at the same time.

Hint: small box appearing under the box pointed by the mouse. It indicates the min and the max values accepted in the box.

I range: current range used in the experiment. It is related to the current resolution.

Impedance: defined by the ratio E/I.

Info: tab in the graphic display that gives the number of points and the size of the raw data file.

Integral: tool available with the graphic display used to integrate curves.

IR compensation: in the electrochemical cell, the resistance between the working and the reference electrode produces a potential drop that keeps the working electrode from being at the controlled potential. IR compensation allows the user to set a resistance value to compensate the solution resistance.

Limits: in the "advanced settings" window, the experiment limits are used in two ways, first to protect the electrochemical cell from damages during the experiment and second for the potential control resolution.

Linear Fit: tool available with the graphic display used to fit a curve as a straight line.

Linear Interpolation: the linear interpolation allows the user to space out regularly each point of the data file. The user can select to interpolate data by a defined number of points or a regular time between each point.

Linked experiments: EC-Lab® offers the ability to link up to ten different experiments with the protocol linker.

Linked experiment settings: the user can save the settings of linked experiments as a .mpls file. This allows the user to easily load all the experiment settings.

LOG: function of the graphic display that opens the log file (.mpl) containing details and settings of the experiment but no data points.

Loop: protocol available in the linked experiments and used to repeat one or more experiments. It is different from the cycle in an experiment.

Low current: option providing a sub-pA resolution that can be added to each channel.
This option extends the current range down to 1 nA. This option can be added both to standard and Z option channel boards.

Min/Max: graphic tool to determine the min and max values on a selected zone of the curve.

Modify: button of the EC-Lab® main window allowing the user to select a protocol, change the experiment parameters (before or during the experiment). This button switches to "Accept" when the user clicks on.

Mott-Schottky: graphic display of $1/C^2$ vs. E_{we} curve and corresponding linear fit to determine slope and offset.

MultiExponetial Sim: this tool can be used to simulate curves with multiexponential functions.

MultiExponetial Fit: this tool can be used to analyze curves with multiexponential functions.

Multi pitting statistics: off-line processing function of the MPP and MPSP protocols that gives the mean values and the mean quadratic deviations of the final rest potentials and the pitting potentials obtained from all the channels used in the experiment.

N'Stat: connection mode used to work with several working electrodes, one counter and one reference electrode in the same electrochemical cell. This mode must be used with special connections (see the user's manual).

N'Stat box: accessory provided for measurement in the N'Stat mode. This box has been designed for multielectrode cell applications to simplify the potentiostat to cell connection.

Open Circuit Voltage (OCV): protocol that consists in a period during which no potential or current is applied to the working electrode. The cell is disconnected and only the potential measurement is available.

Option: EC-Lab® software window in the "Config" menu used to choose general parameters of the software such as automatic data saving or warning messages.

Pause: button of the EC-Lab® main window that leads to a suspension of the progress of the protocol and the measurement recording. The cell is disconnected (OCV period). The "Pause" button switches to "Resume" when clicked.

Peak analysis: graphic tool used on an I(E) curve to determine the peak current, the peak potential, exchanged charge quantity, and several other parameters.

Preconditioning: previous part of the electrochemical experiment that consists of the equilibrium state establishment, deaeration period, accumulation of electroactive species on the electrode surface or pretreatment of the electrode surface.

Process: function in EC-Lab® software made to calculate or extract values of the raw files (.mpr). The new values (in the .mpp file) can be displayed on the graph. The possibilities of processing depend on the protocol used. Please see the description of each protocol in the application part of the user's manual to know the processed values.

Protocol linker: tool of EC-Lab® software used to link protocols in order to build a complete experiment with or without open circuit period between protocols.

Record: in each protocol, the command to define the number of points in the data file. The user can define several recording conditions with potential or charge variation (depending on the galvano or potentio mode) and with time frequency. These data recording option reduces the number of points without loosing any interesting changes in the curve.

Reference electrode: in EC-Lab® software, the user can choose a reference electrode in the list or add his own reference electrode.

Report: file that can be associated with the data file to add additional information.

R_p Fit: tool available with the graphic display used to calculate a polarization resistance.

Run: button that starts the experiment.

Save data: button in the experiment frame that forces the data transfer of the selected channel buffer.

Scan rate: speed of the potential sweep defined with the smallest possible step amplitude.

Selector: window in the graphic display allowing the user to load, add or remove a data file from the graph and to choose the axis parameters.

Specifications: characteristics of the instrument such as cell control or current and potential measurement.

Stern and Geary model: model of corroding systems based on the Tafel equation.

Stop: button used to stop the experiment.

Style: graphic function used to define the plot style and color.

Subtract files: this tool allows the subtraction of two curves, for example to subtract a background from a curve.

Summary per protocol and cycle: off-line processing function giving a table off the maximum and minimum charge, current and potential value for each cycle or loop both in the anodic and cathodic side.

Synchronize: option used in a multichannel mode to start the same experiment at the same time on all the selected channels.

Tafel Fit: tool available with the graphic display used to determine the corrosion current, the corrosion potential and the polarization resistance with a fit.

Tafel graph: off-line processing function allowing the user to display on the graph the logarithm of the current (Tafel plot).

Technique builder: section of the selection technique window including the tools and techniques used to create linked experiments.

Triggers: option that allows the instrument to set a trigger out (TTL signal) at experiment start/stop or to wait for an external trigger in to start or stop the run.

Units: graphic function used to modify the axis units.

VASP Fit: tool available with the graphic display used to fit a curve obtained with the Variable Amplitude Sinusoidal microPolarization technique. This tool is used to determine the current corrosion and the coefficients of corrosion.

Wave analysis: graphic tool used on curves obtained in a convective regime and returning the limit current and the half wave potential.

ZsimpWin: software delivered by PAR and used to fit impedance curves with electrical circuits.

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